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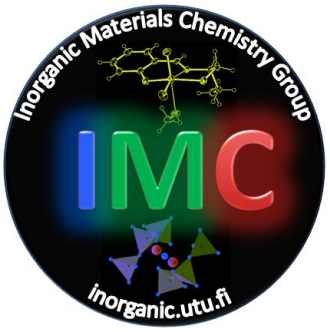

Syntheses and Activities of Vanadium-based Catalysts for the Coupling of CO_2 and Epoxides

Master's Thesis

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Preface

This thesis work is carried out at the laboratory of Inorganic Materials Chemistry Group, University of Turku, Finland.

The basis of this research originally stemmed from my passion for developing better solutions for solving global warming issues and dealing with greenhouse gases, specifically carbon dioxide. By coincidence, I had the chance to see the special report of IPCC (Intergovernmental Panel on Climate Change) in 2017, the headline of ‘‘Global Warming of 1.5ºC’’ struck me. Most land regions are experiencing greater warming than the global average, even Finland has experienced +30ºC in recent years. Global warming is a well-known fact, but with all these listed proves, impacts and risk assessments, I realized I have to act on it. The world moved into industrialization with the cost of climate change, most notably the rising atmospheric CO_2. How will we be able to change this as a chemist? It is my passion to not only find out, but to develop tools and break down barriers for the accessibility of future generations.

I would like to acknowledge that I could not have done this without the help of others. Pasi Salonen, Esko Salojärvi, Anssi Peuronen and many other good friends and colleagues for providing me help on academic research. Special thanks to Dr. Ari Lehtonen, he provided guidance on the thesis project with great knowledge and a sense of humour. Also special thanks to Iki lab in Tohoku University, Japan, for the valuable experiences on heavy metal research.

I will remember all the research experiences, being analytical, prudent and the passion for science will last me a lifetime.

Qingan Wang

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Abstract

Cyclic carbonates as derivatives of CO_2 have drawn attention owing to their several industrial applications. This permits the utilization of CO_2 in a greener way, at the same time, challenges the current practice for synthesizing cyclic carbonates and its derivatives.

This thesis mainly focused on the catalytic coupling reaction of CO_2 and epoxides, a new ligand was created in the making of the catalyst. The objective is to design and synthesize a homogeneous single-molecule transition metal catalyst with the new ligand, in particular if the catalyst(s) can have a better performance on the coupling reaction with different epoxides under various conditions.

Hence, the synthesis of new ligand and catalyst will be described here. The reaction parameters were set in permutations to determine the ideal reaction conditions. Reaction mechanisms are proposed to explain the experimental observations. Repeatable and stable molecules are able to be synthesized by detailed processes.

Keywords: transition metal, homogeneous catalysis, catalytic, coupling reaction, epoxide

Abbreviations

CHO	Cyclohexene
CH_4	Methane
$Co(acac)_2$	Cobalt(II) Acetylacetonate
$CoBr_2$	Cobalt(II) Bromide
$CoCl_2 \cdot 6H_2O$	Cobalt(II) Chloride Hexahydrate
DMSO	Dimethyl Sulfoxide
GHG	GreenHouse Gas
IPCC	Intergovernmental Panel on Climate Change
MeCN	Acetonitrile
MeI	Methyl Iodide
MOF	Metal-Organic Framework
NO_x	Nitrous oxide
PVP	Polyvinylpyrrolidone
SO	Styrene Oxide
TBAB	Tetra-Butyl-Ammonium Bromide
TON	Turnover Number
TOF	Turnover Frequency
$VO(acac)_2$	Vanadyl Acetylacetonate
$VOSO_4 \cdot 5H_2O$	Vanadyl Sulfate Pentahydrate
$VO(O\text{-}iPr)_3$	Vanadium(V) trisisopropoxide oxide

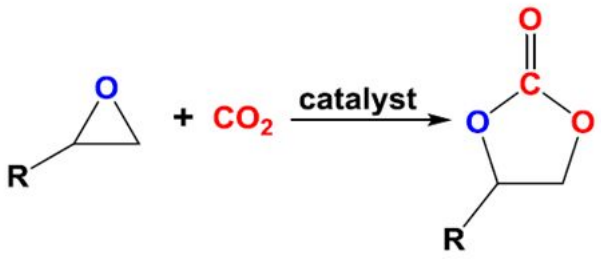
1. Introduction

Throughout the decades, one of the greatest impacts on earth is the global warming brought on by GreenHouse Gases (GHG) such as CO_2, CH_4, NO_x, and O_3. Among all GHGs, of which CO_2 emission has become a global problem. According to the latest data reported with the Intergovernmental Panel on Climate Change (IPCC), compared to pre-industrialization, the concentration of CO_2 in the earth's atmosphere has increased tremendously. The IPCC reports, the global climate has changed relative to the pre-industrial period, the increase in average temperature is 1.5ºC and rising. [1] On average every year, human activities bring 24 billion tons of CO_2 to the atmosphere, in which 22 billion tons comes from the burning of fossil fuel alone. [2] Although the planet has its natural process of removing CO_2 by photosynthesis of the greens, the growing emissions cannot be handled completely by the limited processing capacity of earth.

It is for sure that such enormous CO_2 emission goes past the balance of nature. CO_2 as a cheap, abundant and non-toxic carbon source where it can be easily obtained has caught the interests of scientists all over the world. Researching CO_2 utilization has multiple benefits, on the one hand, to decrease CO_2 concentration in the atmosphere, develop clean energy may reach at emission equilibrium, on the other hand, CO_2 can be converted into many valuable chemicals and fuels like cyclic carbonates or diesel. From the point of view of carbon utilization and environmental protection, research topics of using CO_2 to produce polycarbonates or cyclic carbonates through the reaction between CO_2 and epoxides has been one of the most popular of all time. [3-7]

Polycarbonates are high molecular polymers containing carbonate groups in the molecular chain. Due to the properties of easily worked, molded and thermoformed, polycarbonate has become one of the most used engineering plastics. Polycarbonates manufactured by copolymerization of CO_2 and epoxides has become one of the best solutions to solve the pollution issue of nonbiodegradable plastics. [8] Polycarbonates also have various industrial usages, it can be implemented as adhesives, coatings, ceramic binders, insulation foams and more. [9]

Cyclic carbonate is a cyclic compound which contains carbonate group, it is extensively used in the extraction and separation of mixtures, textiles, electrolytes, fuel additives, intermediates for organic synthesis and the raw materials for plastic due to their excellent physical and chemical properties such as high solubility, high boiling point, low toxicity and degradability.



Scheme 1. Catalytic coupling of CO_2 and epoxides.

The coupling reaction of CO_2 and epoxides is one of the effective and well-known methods for cyclic carbonate formation. Scheme 1 shows the reaction mechanism of coupling of CO_2 and epoxides, under the presence of a catalyst (sometimes a co-catalyst may exist as well), the epoxide is converted into a cyclic carbonate.

Cyclic carbonates as derivatives of CO_2 have shown growing demand in industrial use. Cyclic carbonates are important compounds used as excellent polar aprotic solvents and it has industrial applications such as electrolytes in lithium ion batteries, thickeners of cosmetics, [10-12] as well as its physical properties such as high durability, high transparency and heat resistance, make them the ideal material for applications in the automotive, medical and electronics industries. [13]

1.1 Catalytic Reactions

The coupling of CO_2 and epoxides is one of the most used and important methods for the utilization of CO_2 due to the fact that this reaction has an ideal atom economy and high product yields. [14] With the growing demand of cyclic carbonate, scientists have been researching on the best ways to produce it. The coupling reaction has developed over many decades, catalytic coupling of CO_2 and epoxides to form cyclic carbonate is an important reaction that has received high interests.

Catalysts increase the rate of a reaction and reduce the activation energy, but do not participate in the reaction, so the amount of a catalyst remains unchanged throughout the reaction. With the presence of a catalyst, reaction requires less energy to reach the transition state, it results in more molecular interactions to achieve that state.

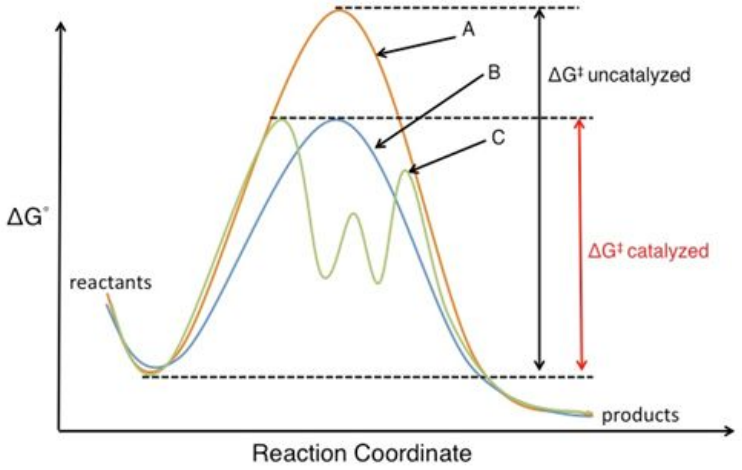


Fig.1 Catalytic Reaction Coordinate. [15]

The difference in Gibbs free energy (ΔG) illustrates how catalyst affects the reaction. The value $\Delta G^{\ddagger}$ influences the reaction rate. In Fig.1 it shows the energy profile for 3 scenarios (A) Uncatalyzed (B) Catalyzed (C) Catalyzed with discreet intermediates (transition states). The scenario A where reaction goes without catalyst, requires the highest activation energy and thus having the highest reaction profile; Scenario B where it has catalyst involved, the activation energy got reduced and it allows a faster reaction rate; Scenario C where a discreet intermediate is involved and catalyzed, usually happens with homogeneous metal-based catalysts, when molecules or ions are coordinated with the metal through intermediate complexation, they tend to accelerate the reaction.

Catalyst as the key substance of a coupling reaction, it can be classified into homogeneous and heterogeneous catalysts, depending on whether they are in the same phase or different phase as the reaction mixture. Phase distinctions are not limited to the generally known solid, liquid, and gas phases, but it also includes immiscible mixtures such as oil and water, or anywhere an interface is present.

The two catalytic systems have many differences in appearance, testing technology, theoretical interpretation and industrial application, but they are some common points still. For example, certain types of chemisorption in heterogeneous catalysis are now understood as the coordination of reactant molecules on metal atoms or ions in homogeneous coordination catalysis. The transfer of adsorbed molecules between the surface active centers of the solid catalyst is similar to the migration of ligands on the transition metal clusters as homogeneous catalysts. [16] Therefore, heterogeneous catalysis has been described using the chemical principles used in homogeneous catalysis.

As new catalysts have been researched and developed, it is important to quantify the catalytic activities to differentiate catalysts, and this is when TON and TOF comes in. The turnover number TON represents the maximum use of a catalyst by means of number of molecular reactions or reaction cycles before getting deactivated. The turnover frequency TOF is a value that quantifies the specific activity of a catalytic centered reaction, it is defined by number of molecular reactions or catalytic cycles per unit time, is it a very useful value to see the efficiency of a catalyst. For most relevant industrial applications the TOF is in the range $10^{-2} – 10^{2}$ s^{-1}. [3]

Heterogeneous Catalysis

Heterogeneous catalysis is the type of catalysis where the catalyst and reactants or products are in different phases. [17] It is different compared to homogeneous catalysis where the reactants, products and catalyst are existing in the same phase. Heterogeneous catalysis generally involves solid phase catalysts and gas or liquid phase reactants. [18]

A heterogeneous catalyst typically is a porous material. A solid phase heterogeneous catalyst reacts in four steps: diffusion, adsorption, reaction and desorption. For gas-solid phase heterogeneous catalytic reactions, it mainly consists of five steps:

- The reactant molecules diffuse from the bulk fluid to the outer surface of the catalyst.
- The reactant molecules diffuse from the outer surface of the catalyst to the inner surface of the micropore.

- The reactant molecules are adsorbed to the inner surface of the catalyst.
- The adsorbed reactant molecules undergo a surface reaction on the inner surface of the catalyst and are converted into products.
- The product molecules after the reaction are desorbed from the inner surface of the catalyst and diffuse back to the bulk fluid in the reverse order.

During the adsorption step of the catalysis reaction, reactions on the catalytic surfaces are of extreme importance for heterogeneous catalysis. The mechanism for these reactions are generally described as $X + Y \rightarrow Z$, the two major accepted interpretations to the mechanism is:

- **Langmuir-Hinshelwood mechanism** [19]: reactant molecules X and Y, both are adsorbed to the catalytic surface, reaction combines them to form product molecule Z, then desorbs.
- **Eley-Rideal mechanism** [20]: reactant molecule X adsorbed to catalytic surface, Y reacts with X without adsorbing to the catalytic surface to form Z, product molecule Z is then desorbed from surface.

The catalyst after reaction, remains its catalytic activity to some extent before it deactivates, its free to mediate further reactions. Most heterogeneously catalyzed reactions belong to the scope of Langmuir-Hinshelwood mechanism. [19]

When choosing the suitable catalysts for heterogeneous catalysis, it is best to remove internal diffusion limitations. When the internal diffusion limitation exists, the internal diffusion step becomes the speed-controlled step of heterogeneous catalytic reaction process. Since the key step in a heterogeneous catalysis is the diffusion of the reactant, and the effective diffusion is more related to the pore structure of the catalyst, thus any of the catalyst evaluation results cannot fully reflect the intrinsic properties of the catalyst, it can only reflect the overall effect of pore structure and chemical nature of the catalyst.

Catalysts have to be active and also stable, so it can be used to make these catalytic processes feasible under reaction conditions. Most solid catalysts tend to disperse on to supporting material to increase surface area in order to increase stability. [21] Usually supporting materials are inert, high melting point materials and a small portion of supporting materials can be catalytic themselves as well.

Most supporting materials are porous, for example zeolite [22] (See Fig.2) and with high surface area-to-mass ratio. Porous supporting material is preferred for the heterogeneous type of catalytic process, for the reason being that reactants and products can enter and exit the material freely.

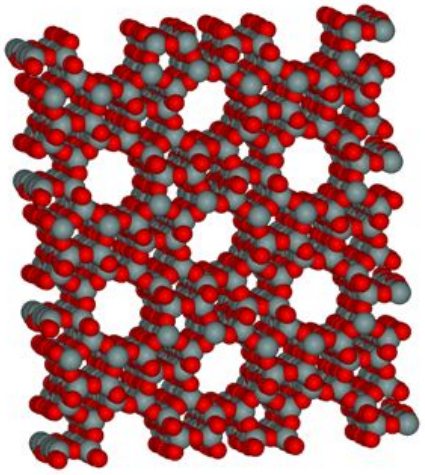


Fig.2 Zeolite ZSM-5 3D structure. [23]

Fig.2 shows the 3D molecular structure of ZSM-5 (Zeolite Socony Mobil-5) type of zeolite. With this structure, only molecules smaller than the crystal pores can enter and exit the catalytic reaction. The zeolite crystal pore size controls the zeolite catalyst. The zeolite catalyst shows great selectivity for the size and shape of the reactant and product molecules. The pore system of ZSM-5 zeolite is a ten-membered ring that has a medium-sized orifice diameter, which makes it having a good shape selectivity.

Heterogeneous Catalyst

The catalyst and the reactant belong to different phases, and the catalytic reaction proceeds at the phase interface. The catalyst used in the heterogeneous reaction system is called the heterogeneous catalyst. Heterogeneous catalysis is one of the catalytic reactions used in coupling of CO_2 and epoxide. Metal-organic frameworks (MOFs) are a classification of a group of complexes which consists of metal ions or clusters that are coordinated to organic ligands, and forming multiple-dimensional structures, they are often porous which makes them great raw material for converting towards a potential porous heterogeneous catalyst.

Li et al. solvothermally synthesized a highly porous heterogeneous catalyst Cu(II)-MOF $\{Cu_2[(C_{20}H_{12}N_2O_2)(COO)_4]\}_n$, the catalyst incorporates both acyl-amide groups and exposed Cu sites, this structure allows it to have a high CO_2 adsorbing capability. [24] When the reaction was changed to a larger sized substrate, the catalytic activity had sharply decreased, this indicated that MOF has a high selectivity against molecular size of the substrate. The MOF has become a highly promising heterogeneous catalyst for CO_2 utilization due to its unique characteristics of having high efficiency and size selectivity.

Conversion of the adsorbed CO_2 to cyclic carbonate was carried out in a Schlenk tube, which contains 20 mmol of epoxide, 0.5 g of co-catalyst of tetrabutylammonium bromide (TBAB) and activated MOF catalyst with 0.08 mmol of Cu sites, under 1 bar pressure of CO_2 at room temperature for 48 h, anhydrous condition. The yields of the generated cyclic carbonates from CO_2 with related epoxides were then compared with benchmark Cu-based MOF, $[Cu_3(btc)_2(H_2O)_3]$, also known as HKUST-1.

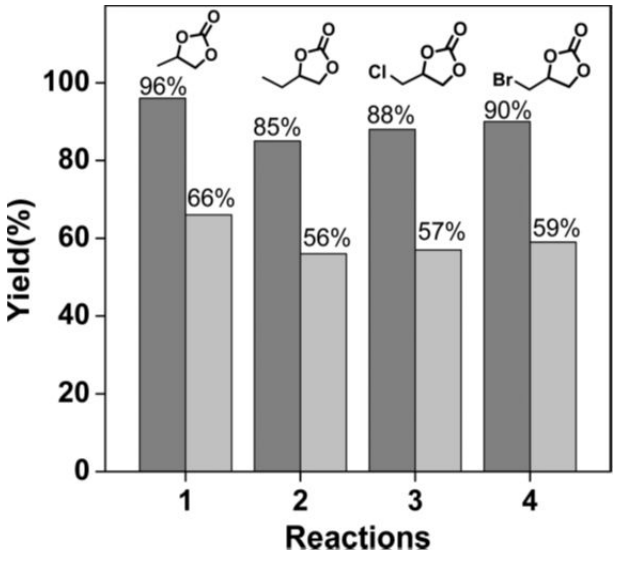


Fig.3 Yields of various cyclic carbonates generated from the CO_2 cycloaddition with related epoxides catalyzed by Cu(II)-MOF (black) and HKUST-1 (gray). [24]

As shown in Fig.3, reaction 1 is for propylene oxide, reaction 2 is for 1-butene oxide, reaction 3 is for 2-(chloromethyl)oxirane, and reaction 4 is for 2-(bromomethyl)oxirane with corresponding TOF values of 10.0, 8.9, 9.2, and 9.4 mol of carbonate per mol of Cu_2 cluster per hour. From the yields of cyclic carbonates, it shows that Cu(II)-MOF has a remarkably higher catalytic performance than HKUST-1 for CO_2 with related epoxides under the same reaction conditions. Both MOF have high porosity and larger surface area, the higher catalytic activity of Cu(II)-MOF should be related to the increase of the CO_2 affinity via the introduction of the acyl-amide groups into the framework.

In addition to the experiments shown in Fig.3, Li et al. also experimented with larger substrates 1,2-epoxyoctane, 1,2-epoxydodecane and 2-ethylhexyl glycidyl ether with yields of 10%, 7% and 6% respectively. The result suggested that smaller substrates could perform in a better state by having good yields (over 80%) while the larger substrates gave substantially lower yields, the cause can be due to the diffusion of these substrates inside the coordination space was difficult.

Homogeneous Catalysis

The catalyst and the reactants are in the same phase, and the reaction without phase boundary exists is called homogeneous catalysis. Homogeneous catalysis is a very active research field, which covers from simple acid-base catalysis to extremely complex enzyme catalysis. The development of homogeneous catalysis is very rapid, and its proportion in the chemical industry has increased rapidly.

Homogeneous catalysts have relatively uniform active centers [25], high selectivity, and few side reactions. It is easy to study the role of catalysts by means of spectroscopy and isotope tracing. Liquid acid-base catalysts, soluble transition metal compound catalysts, and gaseous molecular catalysts such as iodine and nitric oxide belong to homogeneous catalysts. However, homogeneous catalysts have the disadvantage of being difficult to separate, recover and regenerate, easily affected by impurities and poor thermal stability. [26]

Homogeneous catalysts are mostly transition metal complexes, therefore, studying their catalysis has become the mainstream of the development of homogeneous catalysis. Due to the strong coordination ability of the transition metal, it can generate many types of complexes with many ligands. Certain molecules or ions are easy to carry out specific reactions after they are complexed with metals. The role of metals in them is to activate the coordinated reactant molecules through the intermediate complexing step, thereby accelerating the reaction. [27]

Homogeneous catalysis is named after its most significant physical characteristics, that is, the catalyst and the reactants are in the same phase. In fact, most of them are in the liquid phase in coordination catalytic reactions. This feature is distinct from heterogeneous catalysis.

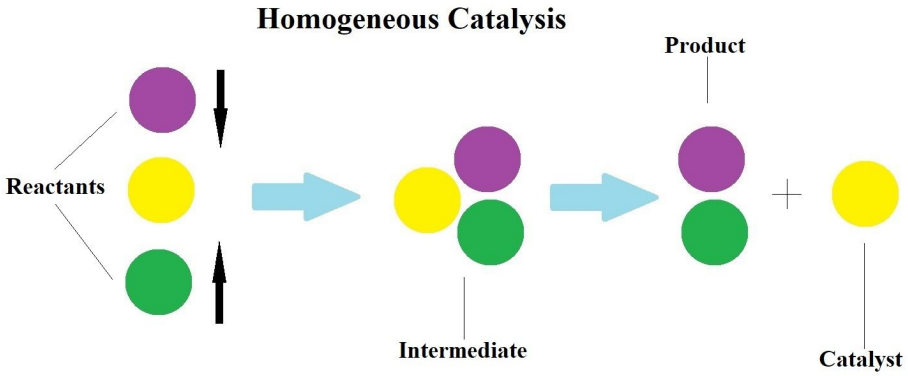


Fig.4 Intermediate product theory.

As shown in Fig.4, two reactants A and B, product AB and catalyst C. The catalytic process can be expressed as:

A + B = AB (slow)

A + C = AC (fast)

AC + B = AB + C (fast)

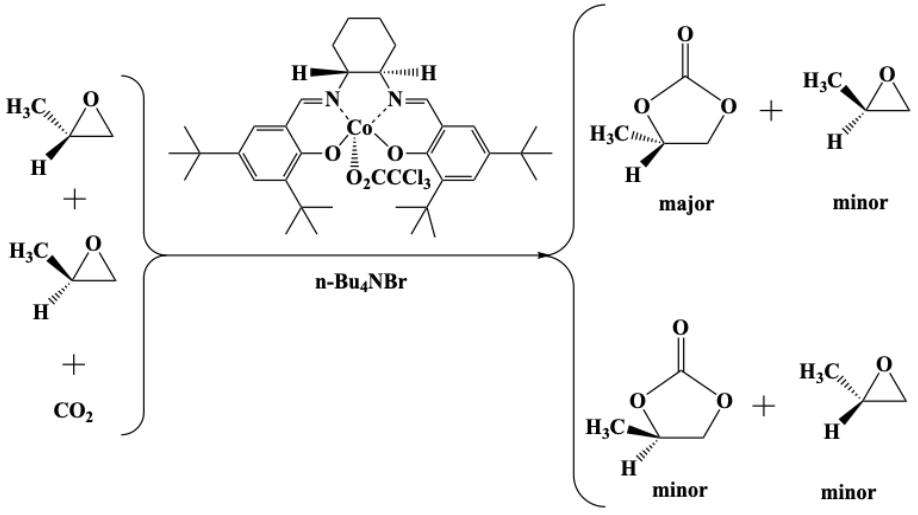
Due to the change of the reaction pathway, the one-step reaction is divided into two steps, and the sum of the activation energy of the two-step reaction is much lower than that of the one-step reaction. This theory is called "intermediate product theory". [28]

In homogeneous catalysis, the catalyst usually combines with reactant molecules or ions to form an unstable intermediate, such as an activated complex. Since the activation energy of this process is usually low, the reaction rate becomes faster, this leads to the intermediate reacts also faster with another reactant (low activation energy applied) to form the final product, and the catalyst is regenerated.

Homogeneous Catalyst

The catalyst that can perform a homogeneous catalysis is a homogeneous catalyst. Homogeneous catalysis is one of the promising and effective methods for the coupling of CO_2 and epoxide. There have been multiple reports of having organometallic complexes as homogeneous catalysts that showed excellent catalytic activity for the synthesis of cyclic carbonates through cycloaddition of CO_2 to epoxides with the aid of a basic co-catalyst. [29-31]

Lu et al. introduced a system for synthesizing optically active cyclic carbonates from racemic epoxides using homogeneous chiral SalenCo(III)/quaternary ammonium halide catalysts. [32] The results shows that under solvent-free condition, the reaction of racemic propylene oxide (0.5 mol) with 0.55 - 0.6 equiv of CO_2, 0.1 mol% of SalenCo(III)(O_2CCCL_3) complex as chiral electrophile and 0.1 mol% of n-Bu_4NBr as nucleophile, experimented 2 hours at room temperature and it could produce a mixture of unreacted epoxide and propylene carbonate with moderate enantioselectivity (See Scheme 2). The formation rate or TOF of propylene carbonate for SalenCo(III)(O_2CCCL_3) complex is up to 245 h^{-1}. A supplementary experiment proved that this homogeneous catalyst has no effect without the co-catalyst, thus a quaternary ammonium salt such as n-Bu_4NBr is essential for this particular reaction.

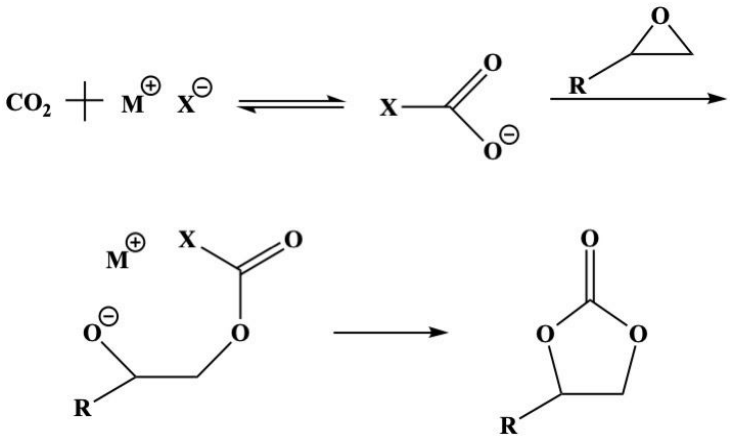


Scheme 2. Racemic Propylene Oxide/CO_2 Coupling. [33]

1.2 Catalytic Coupling of CO_2 and Epoxides

There are many different approaches in the design of a coupling reaction, some uses a catalyst, some don't, but with what has been reported, the most common and effective design is a metal-based catalyst with nucleophile alongside to boost the catalytic activity.

As mentioned in 1.1 that most commonly seen and effective catalysis is with metal catalysts, the generally accepted mechanism which leads to a coupling reaction between CO_2 and epoxides, is through M-O (metal-oxygen) coordination. The first step is CO_2 activation, CO_2 is activated by the nucleophile, then it will interact with epoxide to carry on the catalytic process. The second step is coordination to the metal atom, a portion of electrons from the O atom of epoxide are transferred to the metal ion, this will force the weakening of C-O bond of the epoxide. The weakened C atom of the epoxide is then attacked by the nucleophile from the catalyst to result in the opening of the epoxy ring. After the opening of the epoxy ring, the O atom from the activated CO_2 attacks the positively charged C atom of the epoxide, this leads to the final step, generation of cyclic carbonate, when the process is over, the epoxy ring closes (See Scheme 3). Although the nucleophile itself can catalyze the reaction alone, being incorporated with a metallic complex will make the epoxy ring opening procedure much less energetically demanding and make the subsequent step of CO_2 insertion easier. [33]



Scheme 3. Coupling with CO_2 and epoxide reaction mechanism.

Meiceli et al. [34] came up with a hypothesis that the underlying coordination of the epoxide to the metal center is followed by the ring opening of epoxide which is then mediated by an external (halide) nucleophile. This is a special epoxide-activation mode compared to epoxide activation by a Lewis acid and an external nucleophile which is generally proposed as an intermediate theory in the formation of cyclic carbonate.

1.2.1 Nucleophiles

In the reaction mechanism of coupling reaction of CO_2 and epoxide, the first and foremost step is the activation of CO_2 by a nucleophile. The word nucleophile derived from nucleus and the Greek word φιλος, philos for love. Together it means the favorite of the nucleus and it generally refers to nucleophilic chemical reagents. It is used to measure the strength of a reagent's ability to give electrons, and it is expressed as : Nu. Some molecules or negative ions with unshared electron pairs are called nucleophiles when they react with positively charged carbon. The so-called nucleophile is an electron pair donor, because it can donate its lone pair of electrons, according to Lewis acid-base theory, nucleophile is Lewis base. In the course of the reaction, nucleophiles tend to combine with electropositive species, because the nucleus is electropositive, so "nucleophilic" refers to pro-electron positive.

In polar reactions, nucleophiles provide electron pairs with higher energy for the formation of new bonds. The electron pair of the nucleophilic reagent may be an unshared electron pair or negative charge on the nucleophilic atom, or it may be derived from the heterolytic fission of the σ bond or π bond of the reagent molecule. According to how nucleophiles provide electron pairs, nucleophiles are divided into three types: lone-pair nucleophiles, σ-bond nucleophiles and π-bond nucleophiles.

Lone-pair nucleophiles

There are unshared electron pairs on the nucleophilic atoms of nucleophiles, which can be used to form new bonds with the electrophiles. For example, in Scheme 4 amines provide electrons as unshared electron pair nucleophiles and form bonds with electrophiles. In addition to amines, common unshared electron-pair nucleophiles include alcohols, thiols, alkoxy anions, and carbon anions.

Scheme 4. Unshared electron pair type.

σ-bond nucleophiles

When a covalent bond is formed between a non-metallic atom and a metal atom, the non-metallic atom generally has a large electronegativity, so that the non-metallic atom has a partially negative charge and the metal atom has a partially positive charge. In a polar reaction, the covalent bond between non-metallic atoms and metal atoms in such compound molecules can undergo heterolytic fission. Non-metallic atoms act as nucleophilic atoms with bonding electron pairs to participate in the reaction, so this type of nucleophile is named σ-bond nucleophiles.

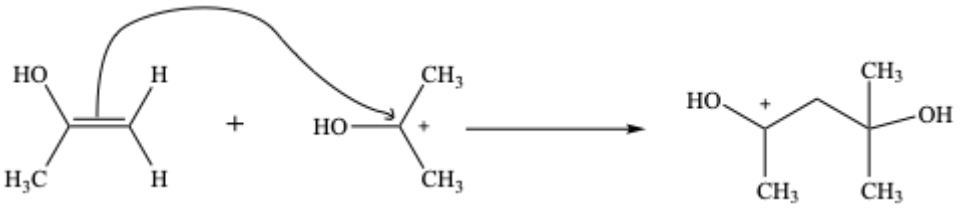
For example in Scheme 5, when lithium aluminum hydride reacts with a carbonyl compound, the Al—H bond in the lithium aluminum hydride molecule undergoes heterolytic fission, and hydrogen carries a nucleophilic addition to the carbonyl carbon with the bonding electron.

Scheme 5. Nucleophilic addition.

The nucleophilic atoms of the σ-bond nucleophile can be heteroatoms (such as $NaNH_2$ or KOH), carbon atoms (such as RMgBr, RLi, and R_2CuLi) or hydrogen atoms (such as $NaBH_4$ and $LiAlH_4$). However, the strong polar bond between non-metallic atoms and metal atoms (Nu-M) is often regarded as an ionic bond (Nu^-M^+).

π-bond nucleophiles

The π bond is used to form a σ bond with the electrophilic atom of the electrophile. For example, the π bond of an alkene can undergo heterolytic fission in the reaction, and one of the double-bonded carbon atoms carries a bonding electron pair to react with the electrophile (See Scheme 6). Therefore, electron-rich olefins are nucleophiles.



Scheme 6 Heterolytic fission of π bond.

When the nucleophilic reagent olefin reacts with the electrophilic reagent, the double bond carbon with a high electron cloud density always forms a new bond with the electrophilic reagent. For pure alkyl-substituted olefins, less substituted carbons have strong nucleophilicity and preferentially combine with electrophiles.

Relationship with basicity

Because the nucleophile provides electrons in the reaction, according to Lewis acid-base theory, the electron donor is regarded as a base. Therefore, the nucleophile is generally basic. Many nucleophilic reactions take place under basic conditions, and it is important to understand the relationship between nucleophilic and basic properties. The nucleophilic strength of nucleophiles is usually measured by the rate at which they react with electrophiles. In many cases, substances with high basicity are also highly nucleophilic. For example, amines are both more basic and nucleophilic than alcohol. Another example, the basicity of phosphine is weaker than amine, but the nucleophilicity is stronger than amine.

As a rule of thumb, the higher the electronegativity, the stronger the nucleophilicity, the stronger the nucleophilicity of the ions, the more appreciable the yield and the speed of the chemical reaction can happen. Based on this prerequisite, the best nucleophiles of all the elements are coming from the halogens group due to its high electronegativity. It should be noted that diatomic forms are not nucleophilic (e.g. I_2 is not a nucleophile), and the nucleophilicity in polar protic solvents $F^- < Cl^- < Br^- < I^-$ and in polar aprotic solvents $F^- > Cl^- > Br^- > I^-$.

1.2.2 Metal-based Catalysts

The metal catalyst is a solid catalyst whose metal is the main active component. Mainly precious metals and transition metals such as iron, cobalt and nickel. Metal catalysts are an important class of industrial catalysts. Mainly include bulk metal catalysts, such as electrolytic silver catalysts, molten iron catalysts, platinum mesh catalysts, etc.; dispersed and supported catalysts, such as Pt-Re- / η-Al_2O_3 reforming catalysts, Ni / Al_2O_3 hydrogenation catalysts; alloy catalysts, intermetallic compound catalyst; metal cluster catalyst.

Classified by whether the active component of the catalyst is supported on the carrier:

Unsupported metal catalyst

Refers to a metal catalyst without a carrier, which can be divided into single metal and alloy according to its composition. It is usually applied in the form of metal skeleton catalyst metal, wire mesh, metal powder, metal particles, metal flakes and metal evaporation film. The metal skeleton catalyst is to make a metal with catalytic activity with aluminum or silicon into an alloy, and then dissolve the aluminum or silicon with a sodium hydroxide solution to form a metal skeleton. The most commonly used metal skeleton catalyst in the industry is skeleton nickel, which was invented by M. Raney of the United States in 1925, so it is also known as Raney nickel. Skeletal nickel catalysts are widely used in hydrogenation reactions. Other skeleton catalysts include skeleton cobalt, skeleton copper and skeleton iron. Typical metal wire mesh catalysts are platinum meshes and platinum-rhodium alloy meshes, which are used in the process of ammoniation to produce nitrification.

Supported metal catalyst

The catalyst on which the metal component is supported is used to improve the dispersion and thermal stability of the metal component, so that the catalyst has a suitable pore structure, shape and mechanical strength. Most supported metal catalysts are prepared by impregnating metal salt solutions on a support, reducing them by precipitation transformation or thermal decomposition. One of the keys to preparing supported metal catalysts is to control the heat treatment and reduction conditions.

According to the active component of the catalyst is one or more metal elements:

Single metal catalyst

Single metal catalyst refers to a catalyst having only one metal component. For example, the platinum reforming catalyst first used in industry in 1949, the active component is a single metal platinum supported on η-alumina containing fluorine or chlorine. Uses such as: rhodium as a catalyst for the exhaust emission control of the automotive industry and the synthesis of phosphorus complexes, hydrogenation reactions and hydroformylation (i.e. carbonylation). Platinum is used as a catalyst in the contact method to produce sulfuric acid, and platinum mesh catalysts are used in ammonia oxidation to produce nitric acid.

Polymetallic catalyst

The components in the catalyst are composed of two or more metals. For example, platinum-rhenium and other bis(poly)metal reforming catalysts supported on γ-alumina containing chlorine. They have more superior performance than the foregoing platinum-only reforming catalysts. In this type of catalyst, multiple metals supported on a carrier can form binary or multi-component metal atom clusters, making the effective component greatly dispersed and improved. The concept of metal atom cluster compounds was first derived from complex catalysts. When applied to solid metal catalysts, it can be considered that there are also several, dozens or more metal atoms clustered on the metal surface.

Characteristics of transition metal catalysts

1) The d-electron layer of the metal cation in the transition metal oxide is easy to lose electrons or capture electrons, and has strong redox performance.

2) The transition metal oxide has semiconductor properties.

3) The internal valence orbit of the metal ion in the transition metal oxide can be cleaved from the foreign orbit.

4) Both transition metal oxides and transition metals can be used as redox catalysts, and the former is more conducive to catalyst performance modulation due to its heat resistance and strong toxicity, as well as photosensitivity, heat sensitivity and impurity sensitivity, so it is used more extensive.

Many metals can be used as catalysts, the most commonly used is the transition metals. Transition metals have excellent hydro-dehydrogenation characteristics and are widely used in the industry as hydro-dehydrogenation catalysts. Some metals also have oxidation and reforming properties. Incorporation of co-catalysts into metal components, or having the metal components dispersed on the support, which are two commonly used types of metal catalysts. Alloy catalysts composed of more than two metals are of great significance for theoretical research and practical applications.

The chemical properties of transition metals are closely related to the d orbital of transition metal atoms. The fraction (d%) of d orbits participating in the formation of metal bonds has a certain relationship with the catalytic activity of metals. In view of the high delocalization of metal-bonded electrons, the electron mobility as a whole property of metal and the long-range electronic interaction between metal atoms should be considered first when studying metal catalysis.

An example of d% by using metal nickel.

e.g. Ni $3d^8 4s^2$ Suppose: d^2sp^3 (30%), d^3sp^2 (70%)

d^2sp^3 ‡ † † ⊖ ⊖ ⊖ ⊖ ⊖ ⊖ d%=2/6=0.33

d^3sp^2 ‡ ‡ ⊖ ⊖ ⊖ ⊖ ⊖ ⊖ ○ d%=3/7=0.43

Total: 0.33×30% + 0.43×70% = 40%. The empty orbit is also a bonding orbit.

The electrons of metal atoms are divided into two types. Bonding electrons are used to form metal bonds. The other type is called atomic electrons or lone-pair electrons. They do not affect the formation of metal bonds, but are related to magnetic and chemical adsorption. In other words, transition metals have two types of orbitals, bonded orbitals (spd), and non-bonded orbitals (or, atomic orbitals). In addition to accommodating lone-pair electrons in the atomic orbit, d cavity (empty part in d orbitals) also exists.

As d% increases, d cavity decreases correspondingly, and the adsorption capacity also decreases. The greater the degree of coordination unsaturation, the greater the chemical effect of external adsorbed molecules. For metal catalysts, an atomic group (atomic cluster) composed of a certain number of surface atoms can be used. The use of the concept of atomic cluster active centers in metal catalysis will enable the communication of the three major areas of heterogeneous, homogeneous and metalloenzyme catalytic activities.

Catalytic system

Due to the thermodynamic properties of carbon dioxide that is relatively stable, it is difficult to directly react with other substances, so it is necessary to introduce a catalyst to promote the catalytic reaction of carbon dioxide and epoxide. Currently, the most studied catalyst systems include zinc catalyst systems, porphyrin catalyst systems, and SalenMX catalysts system, rare earth catalyst system, double metal cyanide catalyst system, supported catalyst system, other catalyst systems, etc.

Zinc catalytic system

The early zinc catalyst system discovered by Beckman et al. [35-37] was obtained from the reaction of $ZnEt_2$ with two or more active hydrogen compounds, namely the $ZnEt_2$-multi-active hydrogen proton compound system. The results show that the single proton source (alcohol , Primary amines, etc.) and dihydroxy proton sources (resorcinol, dicarboxylic acid, etc.) and $ZnEt_2$ can catalyze the copolymerization of CO_2 and PO. On this basis, Kuran et al. [38] found that trihydroxyphenols (pyrogallol, 4-bromopyrogallol) and $ZnEt_2$ can generate PPC at 35 ℃, 6 MPa CO_2 pressure. Through further investigation, it was found that the interaction between the single proton source and $ZnEt_2$ is only propylene carbonate (PC), but contains two or three protons. The catalytic system of the proton source can generate PPC [39,40].

Although the early zinc catalyst system had a single structure and a general catalytic effect, it laid the foundation for the development of the later catalyst system and provided a theoretical basis for the reactions of carbon dioxide and epoxide.

Porphyrin catalytic system

In 1978, Takeda et al. [41] synthesized a series of single-site catalysts based on the tetraphenylporphyrin ligand (tpp) skeleton for the first time (see Fig.5, 1a-1d), and used it for CO_2 and epoxide copolymerization. Studies have shown that at 20 ℃ and 0.8 MPa CO_2 pressure, 1b can catalyze the copolymerization of CO_2 and PO. After 19 days of reaction, the product PPC has a M_n = 3900 g/mol, PDI = 1.15, and a carbonate chain content of 40 %, Although the reaction time is long, it lays the foundation for the development and utilization of porphyrin-based catalytic systems. At the same time, by adding ammonium salt or phosphonium salt in 1d, CO_2 and PO can be catalyzed to form PPC. At 20 ℃, 4.8 MPa CO_2, 1a reacts with $EtPh_3PBr$ to generate PPC. TOF = 0.18 h^{-1}, carbonate chain content is up to 99%.

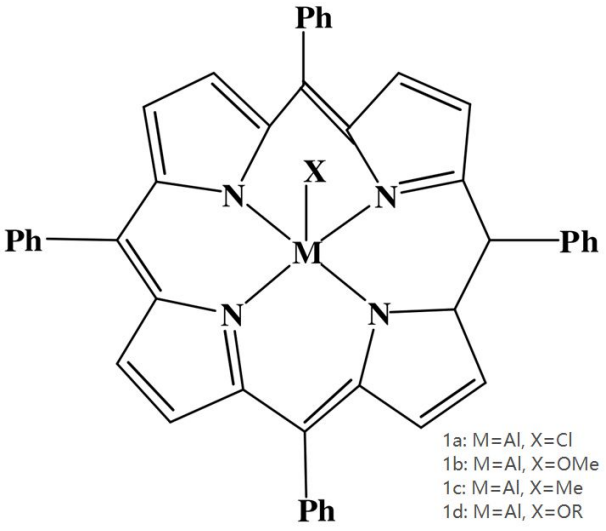


Fig.5 Aluminum tetraphenylporphyrin catalyst.

In 2003, Sugimoto et al. [42] found that [(tpp)MnOAC] can catalyze the copolymerization of CO_2 and CHO. At 80 ℃ and 5 MPa CO_2, the product PCHC was obtained with M_n = 6700 g/mol, TOF = 16.3 h^{-1} , PDI = 1.3, and the content of carbonate links is 99%. When the reaction system is added with co-promoter PPh_3, MeIm or pyridine, it does not promote the reaction, but instead reduces the rate of polymerization and the content of carbonate links.

Yang et al [43] developed a series of highly efficient tetraphenylporphyrin complex TPPCoⅢX (see Fig.6) and used dimethylaminopyridine as a cocatalyst to catalyze the copolymerization of CO_2 and CHO. Under the condition of 1 equivalent of cocatalyst for 6 h, highly selective alternating PCHC was obtained, with a carbonate bond content exceeding 99% and M_n = 59,600 g/mol, which is the most active in the porphyrin-based catalytic system.

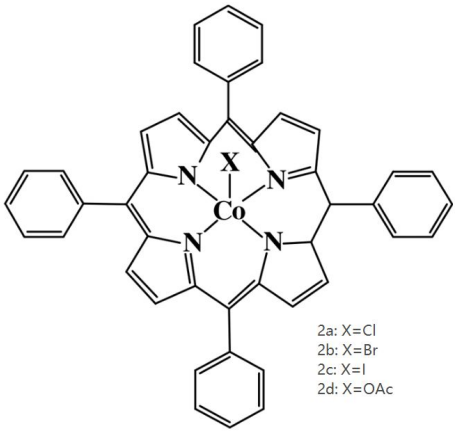


Fig.6 Cobalt tetraphenylporphyrin catalyst

In 2015, Sheng et al. [44] set out to develop a series of bifunctional aluminum porphyrin complexes and tested their copolymerization of PO and CO_2. The results show that the number of methoxy groups in the ligand framework and the alkyl chain of the quaternary ammonium cation are adjusted. The length of the can change the electronic environment of the central Al atom and optimize the catalytic performance of the reaction. Among them, the complex containing six methoxy groups in the ligand framework is the best catalyst. At 80 ℃, 3 MPa pressure, TOF = 1320 h^{-1}, PPC selectivity is 93%, TOF at 90 ℃ and 3 MPa up to 2824 h^{-1} and PPC selectivity remains at 89%.

Compared with other catalytic systems, porphyrin-based catalytic systems have higher preparation cost and longer reaction time, but their biggest advantage is that they can obtain copolymers with narrow molecular weight distribution. At present, mainly by changing the ligand structure, the electron cloud density of metals, Metal type to adjust the catalytic performance of the reaction, while also trying to develop new rare earth porphyrin complexes, to obtain copolymers with high application value.

SalenMX catalytic system

In 2015, the Yb (salen) complex 11 (see Fig.7) / NBu_4Cl researched and developed by Antonello et al. [45] can catalyze the copolymerization of CHO and CO_2 to obtain PCHC under 70 ℃, 2 MPa CO_2 pressure, and PCHC after 18 h TOF = 31 h^{-1}, conversion rate 57%, M_n = 10200 g/mol, PDI = 1.54. Compared with other transition metal / lanthanide salt complexes, the newly proposed catalyst has better activity and copolymerization selectivity.

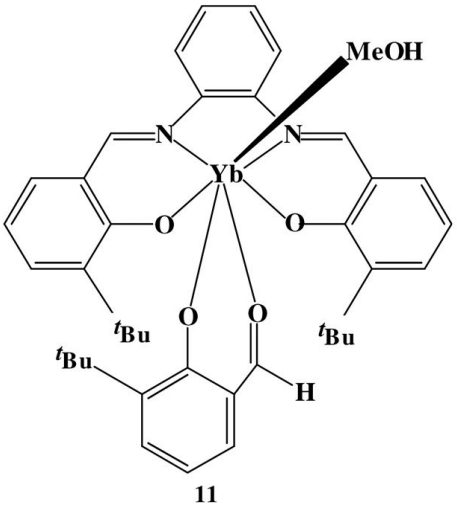


Fig.7 Salen-Yb catalyzed CHO-CO_2 copolymerization

In 2016, the catalyst 12 developed by Cuesta-Aluja et al. [46] (see Fig.8) and the related complexes of Fe, Co and Cr, the catalyst 12 has relatively high activity and can be combined with tetrabutylammonium bromide (TBAB) forming an active binary catalytic system. Under 80 ℃, 1 MPa pressure, it can catalyze the cycloaddition reaction of CO_2 and epoxide, the product TOF = 120 ~ 3434 h^{-1}. Among them, the highest catalytic activity is the cycloaddition reaction of CO_2 and 1-chloro-2,3-propylene oxide, the TOF value is as high as 3434 h^{-1} and kinetic experiments show that this reaction is a first-order reaction. In addition, the catalytic system 12 / PPNCl can catalyze the reaction of CHO and CO_2 to obtain PCHC, M_n = 2900 g/mol, PDI = 1.3.

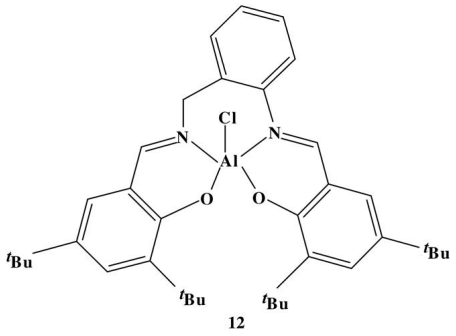


Fig.8 Salen-Al catalyst

In 2016, Wu et al. [47] used (salen)CoX(14)/PPNTFA binary catalyst system (see Fig.9) to explore the mechanism of water in the coupling reaction of PO / CO_2 and CHO / CO_2. The mechanism study of IR and ^1H NMR shows that CO_2 / epoxide copolymerization first hydrolyzes to form diol, so water is not a real chain transfer reagent during the epoxide / CO_2 coupling reaction, Instead, the α, ω-dihydroxy-terminated polycarbonate produced by diol as a chain transfer agent, Therefore, the CO_2-based triblock copolymer is composed of three catalytic reactions: hydrolysis, CO_2 / epoxide coupling reaction and ring-opening polymerization.

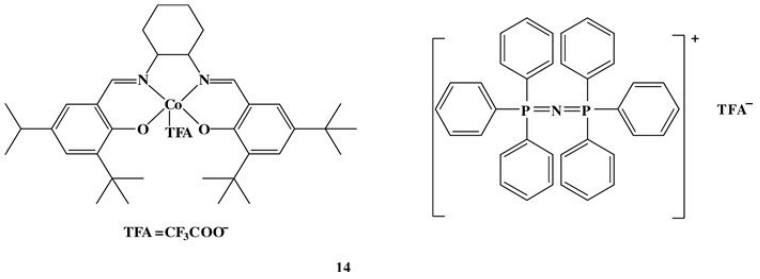


Fig.9. Salen-Co / PPNTFA catalyst

The SalenMX catalytic system is a catalytic system that has been studied more in recent years. At present, the preparation method of this type of catalytic system is simple, the temperature and pressure of the reaction are relatively mild, and the carbonate chain content in the resulting product is high, the molecular weight distribution is narrow and Catalyze multiple reactions. At present, the most researched are the SalenCrX and SalenCoX catalytic systems. By adjusting the ligand structure and axial anion type of this type of catalytic system to change the complex structure, new catalysts can be obtained. Catalytic activity. On this basis, the type of metal can also be changed to develop a new Schiff base catalytic system that is economical and more practical.

Double metal cyanide catalyst system

In 1985, Kruper et al. [48] reported a series of double metal cyanide compounds with the formula: $M_a^1(M^2(CNx))_b$(a and b: 1, 2, 3; x: 4, 5, 6) copolymerization of epoxides, in which zinc hexacyanoferrate (Ⅲ) can catalyze the formation of polycarbonates from EO, PO, 1-butene epoxide and CHO, with carbonate chain content of 50% ~ 95%, PDI = 2 ~ 6, TOF = 4 h^{-1}.

In 2009, Wu et al. [49] prepared a double metal cyanide complex catalyst based on $Zn_3[Co(CN)_6]_2$, and explore the catalytic performance of $Zn_3[Co(CN)_6]_2$ catalyzed PO / CO_2 copolymerization under different reaction conditions and the effect of reaction conditions on product composition. The results show that the catalytic efficiency increases with increasing temperature and decreases with increasing pressure in the range of 80-130 ℃. Therefore, the reaction at a lower temperature and a higher pressure for 10 h is conducive to the conversion of CO_2 to a copolymer.

Zheng et al. [50] studied the copolymerization of CO_2 and PO and the homopolymerization of PO catalyzed by double metal cyanide complex (DMC) catalyst, and explored the induction phenomenon of DMC catalyst. The results show that the induction period of DMC catalysis during copolymerization is shorter than that of homopolymerization, especially at low CO_2 pressure (1.0 MPa). The induction period is shortened from 45 mins during homopolymerization to 15 mins during copolymerization. During the copolymerization, the induction period increases with the increase of CO_2 pressure.When the reaction pressure increases from 1.0 MPa to 7.0 MPa, the induction period increases from 15 to 40 mins. The initiation phenomenon of PO and CO_2 copolymerization is different from that of PO homopolymerization: when the copolymerization is initiated, the temperature and pressure suddenly increase abnormally and quickly decrease to the state before initiation, while the temperature is suddenly increased after the homopolymerization is initiated and then gradually decreases. From this, it can be seen that CO_2 can promote DMC catalyst activation.

Compared with other catalytic systems, the double metal cyanide catalyst system has multiple metal active sites. However, the catalyst structure is more complicated, and the research on the catalytic mechanism is more difficult.At the same time, the selectivity of the product produced is not high, which is also an important factor hindering its development. Therefore, finding a composite catalytic system with simple structure, high catalytic activity, simple separation, high selectivity and short polymerization time has become the focus and difficulty of research.

As previous studies have shown, not every metallic complex is suitable for the coupling of CO_2 and epoxides. [51,52] Williams et al. published a successfully synthesized, bimetallic Co(II) catalysts with TOF = 172 h^{-1} and mixed metallic Co(II)/Co(III) catalysts with TOF = 159 h^{-1}, both were active under CHO/CO_2 condition at ambient pressure. [53,54] Amine-bis(phenolato) catalysts were introduced for the coupling of CO_2 and epoxides for its outstanding results with chromium-based amine-bis(phenolato) complex (See Fig.10). [55–57]

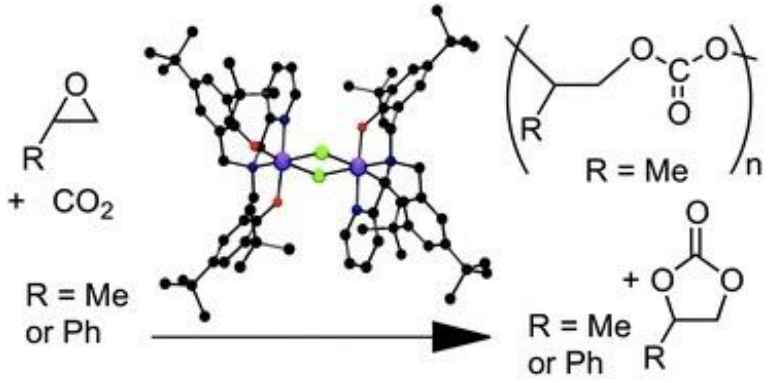


Fig.10 A chromium(III) di-amine-bis(phenolate) complex, {CrCl[O_2NN']^{BuBu}}$_2$ catalyzes the copolymerization of propylene oxide with carbon dioxide. [60]

A paper published by Darensbourg et al. states that the coupling reaction of epoxide and CO_2 to produce cyclic carbonate and/or polycarbonates, are highly dependent on various factors, including the nature of epoxide, the metal catalyst, and the reaction conditions such as temperature and pressure. [58-62]

Among the existing catalytic systems, only Cr, Co and Zn catalytic systems have higher catalytic activity for the reaction of CO_2 with epoxides, but the higher temperature, higher pressure conditions and high cost catalytic systems in the reaction process have been hindering the development.

Vanadium-based homogeneous catalysts have been extensively studied for selective oxidation of various organics, but for the coupling reactions of CO_2 and epoxides, the most commonly studied transition metal includes Zn, Cu, Cr, Co, Mo and some expensive rare metals. As far as we know, the use of vanadium in the formation of cyclic carbonates and related compounds remains rare, with limited application potential. Considering the importance of cyclic carbonates and recognizing the previous efforts in this area, we have attempted to design and synthesize a vanadium-based catalysts with tridentate-amino-bisphenol ligand and substituted ammonium iodide sidearm.

2. Experimental

The original proposal was that the coupling reaction catalyzed by a main catalyst and a co-catalyst that carries nucleophile, the proposal was improved and changed to the coupling reaction with a single-catalyst incorporated with nucleophile. This thesis work is aimed at synthesizing a homogeneous single-molecule vanadium-centered catalyst with tridentate-amino-bisphenol ligand and substituted ammonium iodide sidearm, and to understand its characteristics.

The purpose of this research is to find if the new catalysts can have a better performance on the coupling reaction with different epoxides under various conditions, parameter concerned in this experiment is the reaction time, CO_2 gas pressure, temperature and molar ratio to epoxide. All possible and feasible combinations of all parameters were carried out in a laboratory scale experiment in an autoclave to obtain the best combination of different parameters.

The main procedures can be roughly divided into three parts, where in chapter 2.2 explains the synthesis of tridentate-amino-bisphenol ligand with substituted iodide sidearm, chapter 2.3 explains the formation of the vanadium complexes, and chapter 2.4 explains the coupling reactions with the CO_2 and epoxides.

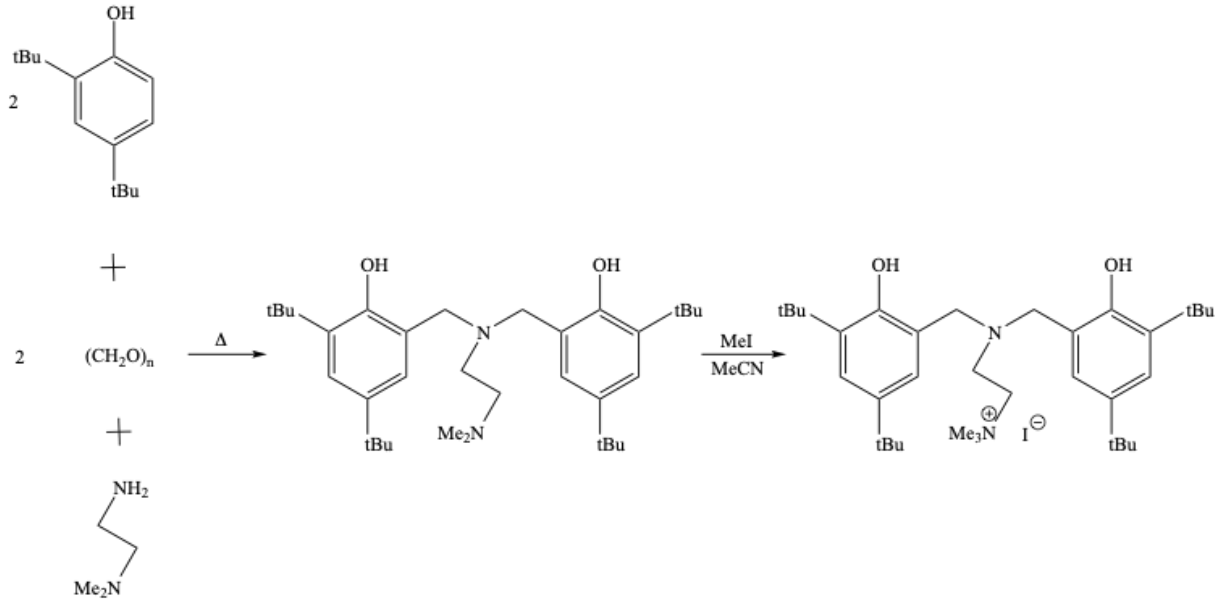
2.1 Equipments and Chemicals

All chemicals used were of reagent-grade quality and obtained from commercial suppliers. Infrared spectra were recorded on a BRUKER VERTEX 70 spectrometer. UV-Vis spectra were recorded on Agilent Cary 60 UV-Vis spectrometer. Mass spectra were recorded on micrOTOF-Q spectrometers. NMR were recorded on TYBruker400 (400 Mhz Bruker AVANCE-III NMR-system). The single-crystal XRD measurements were done by Anssi Peuronen at University of Jyväskylä.

2.2 Synthesis of H_2L

The tridentate-amino-bisphenol ligand with substituted iodide sidearm will be abbreviated as H_2L from here onwards.

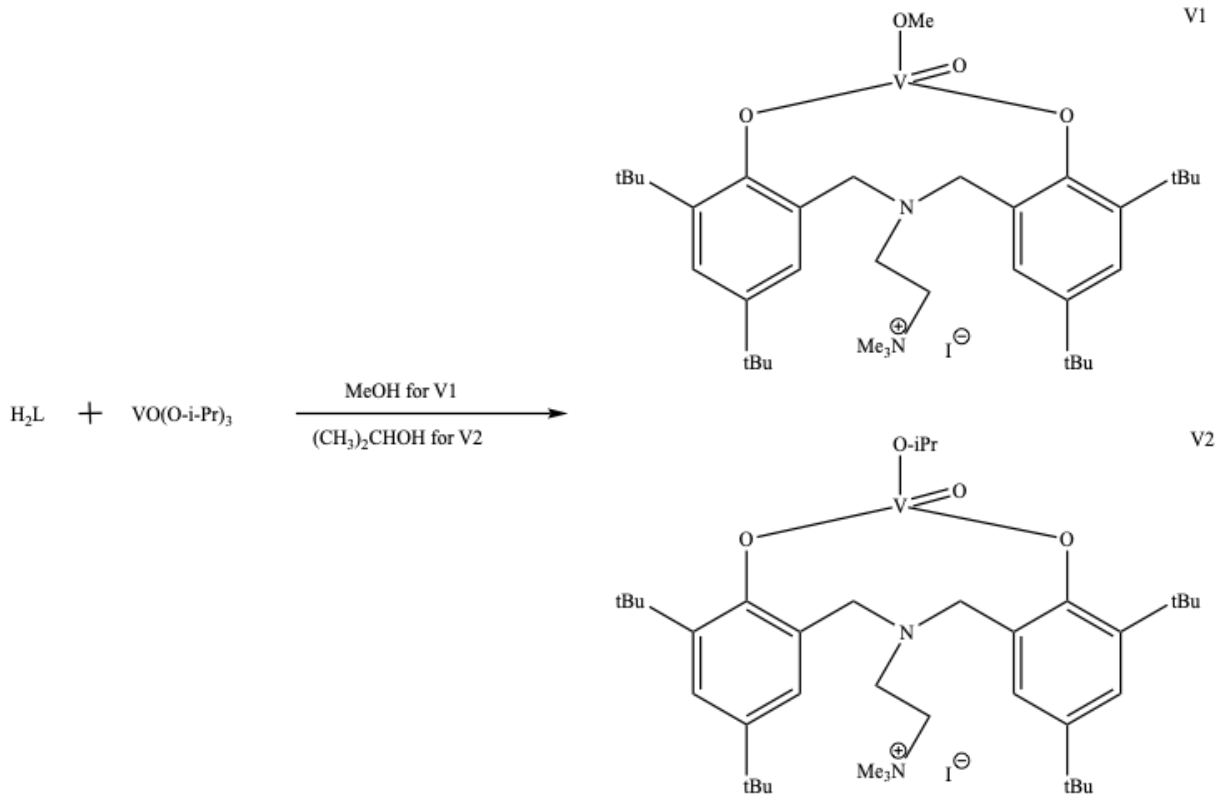
H_2L was synthesized in a two-step reaction. First step was to mix three starting materials, 2,4-di-tert-butylphenol (20 mmol, 4.12 g), paraformaldehyde (20 mmol, 0.6 g) and N,N'-dimethyl-ethylene-diamine (10 mmol, 1.07 ml) in the ratio of 2:2:1, respectively. The mixture was initially in solid state, applied with 100ºC oil bath heating and magnetic stirring, mixture slowly turned into a thick, transparent but slightly yellowish color in liquid state. The mixture became the intermediate product of amino-bisphenol with dimethylamine. The synthesis was continued without isolation, in the second step, methyl iodide (20 mmol, 1.25 ml) and MeCN (ca. 20 ml) were added, where MeCN was used as a solvent, and then the synthesis was refluxed with condenser overnight. After the overnight reflux, the mixture exhibits color between light yellow and milky white. The final product H_2L was isolated by filtration, it exhibits as a white powder and is stable under ambient air (See Scheme 7).



Scheme 7. The synthesis path of H_2L.

2.3 Complexation

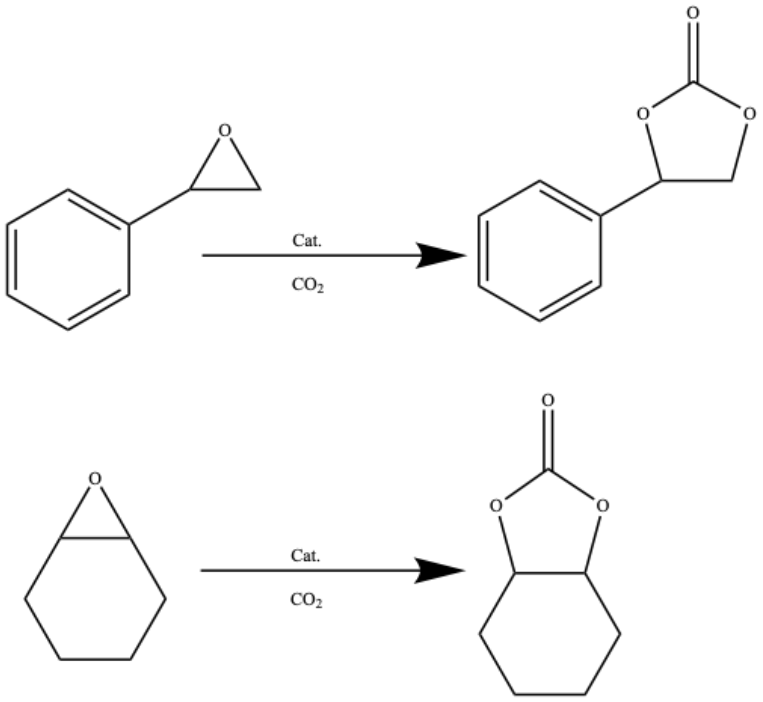
Complexation was with H_2L and Vanadium(V) trisisopropoxide oxide $VO(O\text{-}iPr)_3$. There were two vanadium complexes made in different solvents. The vanadium complexes **V1** and **V2** were synthesized by equivalent amounts of H_2L and $VO(O\text{-}iPr)_3$, using MeOH (ca. 20 ml)(**V1**) or isopropanol (ca. 20 ml)(**V2**) as solvent respectively. H_2L (5 mmol, 3.33g) was dissolved first in solvent until solution became transparent, followed by adding $VO(O\text{-}iPr)_3$ (5 mmol, 1.18 ml) dropwise with a pipette, the whole process applied only magnetic stirring, no heating was needed (See Scheme 8). After thorough mixing, the reaction mixture was concentrated and left to crystallize in the freezer.



Scheme 8. The synthesis path of vanadium complex V1/V2.

2.4 Coupling of CO_2 and Epoxides

The coupling reaction is a type of reaction where two original compounds are joined together with the presence of a catalyst. In this study, the coupling reaction was performed in the presence of a vanadium complex as catalyst, epoxide (SO or CHO), and pressurized CO_2, the aim was to produce cyclic carbonate (See Scheme 9).



Scheme 9. Coupling of CO_2 with epoxides of styrene carbonate and cyclohexene carbonate.

To test out the performance and efficiency of the new catalysts, 4 parameters were chosen, reaction time, CO_2 gas pressure, temperature and molar ratio. Prior to actual coupling reactions, four experiments were tested to find the effects of each parameter on the experimental results and found that the molar ratio had no significant effect on the yield of cyclic carbonate in this experiment, thus all experimental data were with 1 mol% ratio catalyst to epoxide as standard.

Experiments were done in sample sets, where each sample set includes 4 samples. In addition to sample sets, 3 parameters that are interchangeable were used. The 3 parameters were reaction time in hours (3, 9, 15, 21), temperature in ºC (25, 50, 75) and pressure in bars (1, 5, 10). The samples in the sample sets were composed of 4 samples as shown in Table 1. Sample compositions in a sample set, and each sample was named after their codename plus corresponding parameters, for example a sample of vanadium complex V1 and Styrene oxide reacted under 3 hours, 25 ºC, 1 bar condition, the sample would be named V1SO032501.

Table 1. Sample compositions in a sample set

	Styrene Oxide (SO)	CycloHexene Oxide (CHO)
V1	**V1SO**	**V1CHO**
V2	**V2SO**	**V2CHO**

Since the experiment parameters cannot be changed midway, there is only one sample set possible per experiment. A total of 30 experiments, 120 samples have been conducted consecutively in autoclave with different combinations of parameters.

The coupling reactions were done by placing sample sets into autoclave, and autoclave in a heating tank full of water, applied with corresponding parameters. The details of exact combinations of parameters, yields and product status are shown in Table.2 Parameter combinations in coupling reaction, Table.3 Cyclic carbonate yields and Table.4 Samples wet and dry conditions, respectively in the Results and Discussion section.

2.5 Reference Samples

In order to evaluate the performance of the catalyst in coupling reaction, 10 reference samples consisting of styrene carbonate and styrene oxide in different ratios were prepared. The infrared spectra of the reference samples were used to evaluate the yield of each sample after the coupling reaction.

Styrene carbonate was prepared with a known reaction. For the preparation of styrene carbonate, cobalt(III) chloride hexahydrate was used as the main catalyst, tetrabutylammonium iodide as co-catalyst, and styrene oxide as the epoxide. Samples were prepared in coupling reaction, both catalysts were 1 mol% to the epoxide, placed in autoclave, under the condition of 50ºC, 10 bars and overnight reaction (more than 16hours). Detailed compositions of each reference sample are listed in Table 5. Reference Sample Composition in the Results and Discussion section.

3. Results and Discussion

3.1 Synthesis of H_2L

The thesis work was originally planned with having a pro-ligand with bisphenol structure and a metal precursor to synthesize a complex that carries nucleophile, which acts as a catalyst. Metal precursors cobalt(III) chloride hexahydrate $CoCl_2 \cdot 6H_2O$, cobalt(II) bromide $CoBr_2$ and cobalt(II) acetylacetonate $Co(acac)_2$ were tested, of which $Co(acac)_2$ was synthesized in the laboratory. After the test and error of above metal precursors, none of it met the expectations, another approach was introduced.

The H_2L in this experiment were specifically designed for catalytic reactions. At first, the work was to find what combinations would produce a stable single-molecule pro-ligand with bisphenol structure. Several starting materials were used and combinations were tested, these materials can vary from small structural differences, or it is a completely different chemical compound. As mentioned in the Experimental section, synthesizing H_2L was done in a two-step reaction, and the first step was to find the right combination of starting materials to synthesize an intermediate product. In order to find out, several combinations were tested.

The combinations were as follow:

2,4-di-tert-butylphenol + paraformaldehyde + 3-amino-1-propanol.

2,4-di-tert-butylphenol + paraformaldehyde + N,N'-dimethyl-ethylene-diamine.

2-tert-Butyl-4-methylphenol + paraformaldehyde + N,N'-dimethyl-ethylene-diamine.

The intermediate product (amino-bisphenol with dimethylamine) of the reaction 2,4-di-tert-butylphenol + paraformaldehyde + N,N'-dimethyl-ethylene-diamine was found to be the most suitable to carry on the synthesis due to its significant performance that has reached expectation.

Since halide ions usually have a large electronegativity, the higher the electronegativity, the stronger the nucleophilicity, the stronger the nucleophilicity of the ions, the more appreciable the yield and the speed of the chemical reaction can happen. With this theory in mind, methyl iodide (MeI) was used, as it reacts with tertiary amines to form quaternary ammonium iodides, iodide ions have the strongest nucleophilicity in polar protic solvents, it naturally became an ideal nucleophile. MeI and MeCN was added to the intermediate product to carry on the synthesis of H_2L. The synthesis of H_2L was done several times throughout this thesis work due to the relatively large demand for the following processes, a 90% yield as the highest was recorded.

3.2 Complexation

After obtaining a brand new pro-ligand (H_2L), the process carried on to the complexation with metal precursor. In theory, it is only to find a metal precursor that can provide a metal ion to be in coordination with the H_2L to give the result. In this context, all the cobalt precursors used in the previous trials were tested again, $CoCl_2 \cdot 6H_2O$, $CoBr_2$ and $Co(acac)_2$ were experimented, but only two gave results that came slightly positive.

The reaction of H_2L and $CoCl_2 \cdot 6H_2O$ was done in a MeOH solution with the presence of triethylamine. This experiment was unsuccessful on the first crystallization, after washing with MeCN, blue-green solids were obtained. The reaction of H_2L and $Co(acac)_2$ was done in a MeOH solution with the presence of triethylamine. This experiment was successful at first try, but impurities with brown color were present, reaction mixture was washed with n-hexane to dissolve the impurities and pink-colored crystals were collected after isolation.

In addition to the cobalt metal precursors, we considered the vanadium from the same period. Vanadyl acetylacetonate $VO(acac)_2$ was first selected, after reacting with H_2L in MeOH solution, concentrating and recrystallizing several times, there were no crystals obtained that could be used for coupling reaction. Followed with vanadyl sulfate pentahydrate $VOSO_4 \bullet 5H_2O$ and H_2L in MeOH solution, the reaction did not yield any crystals after several times of recrystallization. Last but not least, the reaction with $VO(O\text{-}iPr)_3$ and H_2L in MeOH solution was very successful at first try, crystals were visible after crystallizing overnight in the freezer, crystals and impurities coexist in the reaction mixture, therefore the reaction mixture was washed with n-hexane, larger pieces of impurities were removed manually, dark-colored crystals were collected and yielded around 28%.

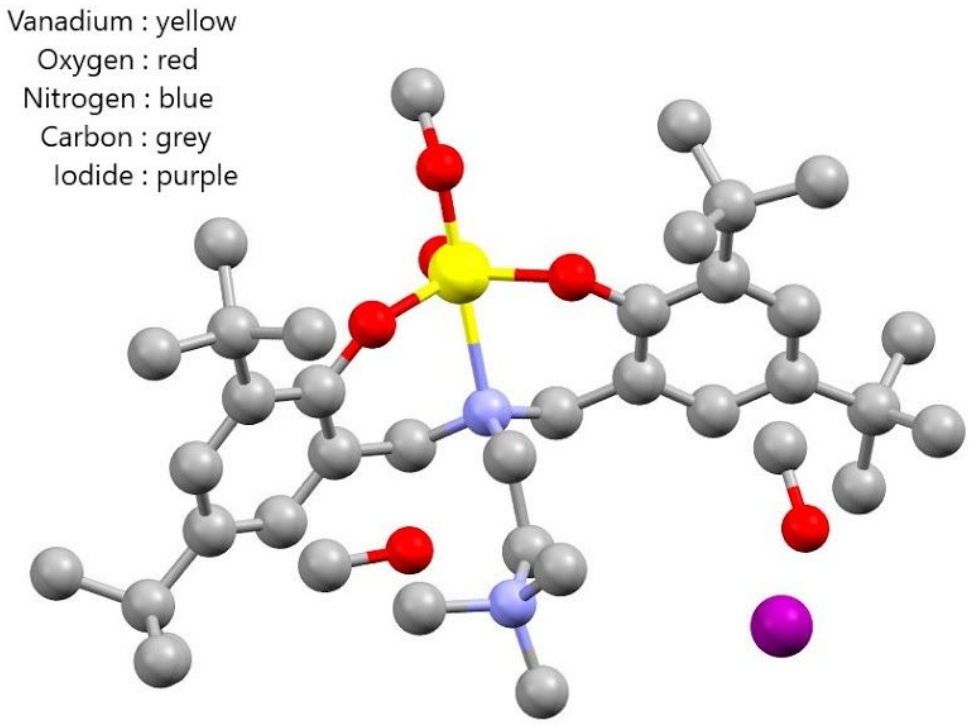


Fig.11 Molecular structure of vanadium complex made in MeOH.

Fig.11 shows the molecular structure of the vanadium complex made in MeOH solution and this complex was later confirmed to be the final product of this thesis work. The complex is in ionic form, the coupling reaction mechanism requires nucleophiles, and it is proven that the iodide ion has strong nucleophilicity due to its electronegativity, hence it exhibits catalytic activity during coupling reaction.

3.3 Coupling of CO_2 and Epoxides

Cyclic carbonate generally contains a carbon-oxygen double bond (C=O), the double bond appears around 1800 cm^{-1} in IR spectroscopy, it is a key indicator to see if there is any cyclic carbonate in the reaction mixture to determine whether the coupling reaction was successful or not.

The products of metal complexes mentioned in the previous chapter were all used as potential catalysts for the coupling reaction with CO_2 and epoxide, a sample with only H_2L was also prepared for the coupling reaction to see if H_2L itself has any catalytic activity. Three samples were prepared for testing their catalytic activities. The three samples were of different metal complexes, one catalogue by blue-green solids from $CoCl_2 \cdot 6H_2O$ reaction, other by pink-colored crystals from $Co(acac)_2$ reaction and the third H_2L sample (named no cobalt in Fig.12) . For all three reactions, styrene oxide was used, and samples were done in the same reaction condition, the reaction parameters were 15 hours, 50 ºC and 10 bars. After the coupling reaction, the IR spectra of all three samples were compared with the reference samples (See Fig.12).

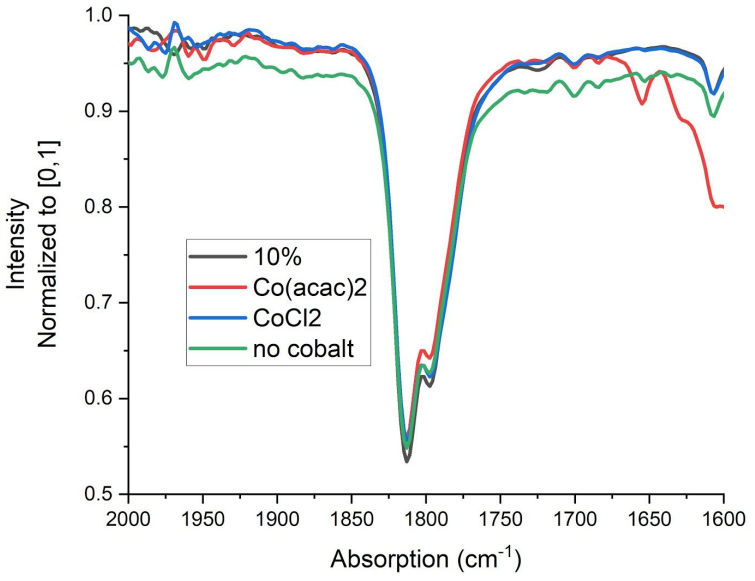


Fig.12 The IR spectra of $Co(acac)_2$, $CoCl_2$ and no cobalt sample compared with 10% reference sample.

The results were that although all samples have crystallized and became one molecular structure, their catalytic capabilities may not have been strengthened or even changed. According to their IR spectra, all the samples exhibited around the 10% yield, which means cobalt ions may not be very reactive in this type of reaction if pro-ligand H_2L itself can catalyze already 10%, and due to this reason, we started to try vanadium complexes.

There are numerous situations in which chemical products are synthesized, we thought maybe that the complexation process would affect the catalytic performance of the metal complexes. Therefore, in-situ experiments (reactions of all ingredients are done in one pot) were done to compare the catalytic performances. The metal precursor, pro-ligand H_2L and styrene oxide were used to prepare samples for in-situ experiments. Two in-situ experiments, one catalogue by $VO(acac)_2$, other by $VOSO_4 \bullet 5H_2O$ were done in autoclave with the condition of 15 hours, 50 ºC and 10 bars, 1 mol% ratio catalyst to epoxide (styrene oxide was used) and overnight reaction time.

The catalytic activities of $VO(acac)_2$ and $VOSO_4 \bullet 5H_2O$ were compared by comparing the IR spectra of the reaction mixture after in-situ experiment to the reference samples. Both in-situ reactions had some yields on cyclic carbonate as they have shown stronger intensity at 1800 cm^{-1} in their IR spectra, for $VO(acac)_2$ it yielded around 15% and $VOSO_4 \bullet 5H_2O$ yielded around 25% (See Fig.13).

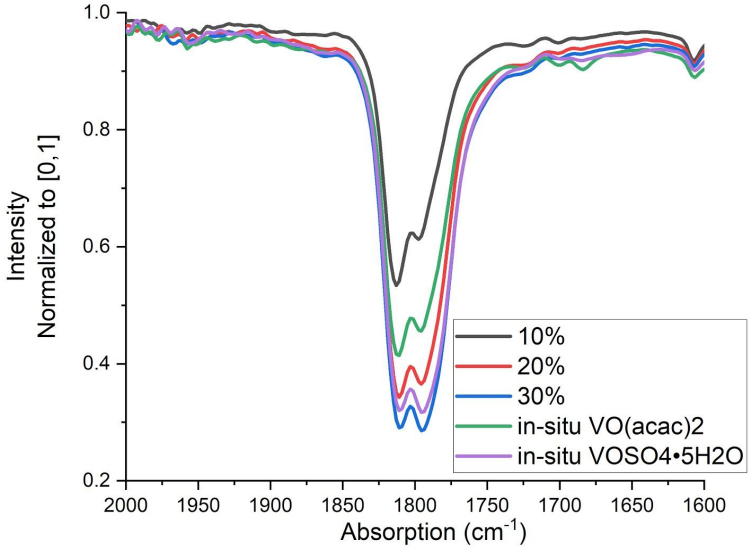


Fig.13 The IR spectra of in-situ $VO(acac)_2$, in-situ $VOSO_4$ compared with reference samples.

Similarly, the catalytic activity of $VO(O\text{-}iPr)_3$ was also compared with reference samples. Both the reaction mixture of coupling reaction of the previously prepared and isolated vanadium complex and the reaction mixture of the in-situ reaction of $VO(O\text{-}iPr)_3$ and H_2L were compared to the reference samples with IR spectra at 1800 cm^{-1}. The findings were that the coupling reaction with vanadium complex can yield up to around 28% after washing the reaction mixture with n-hexane (vanadium complex may not be completely precipitated), and the in-situ reaction can obtain 50% - 60% yield according to IR spectra (See Fig.14). Comparing the two IR spectra, the yields were very similar, and the in-situ reaction yielded slightly higher than the other.

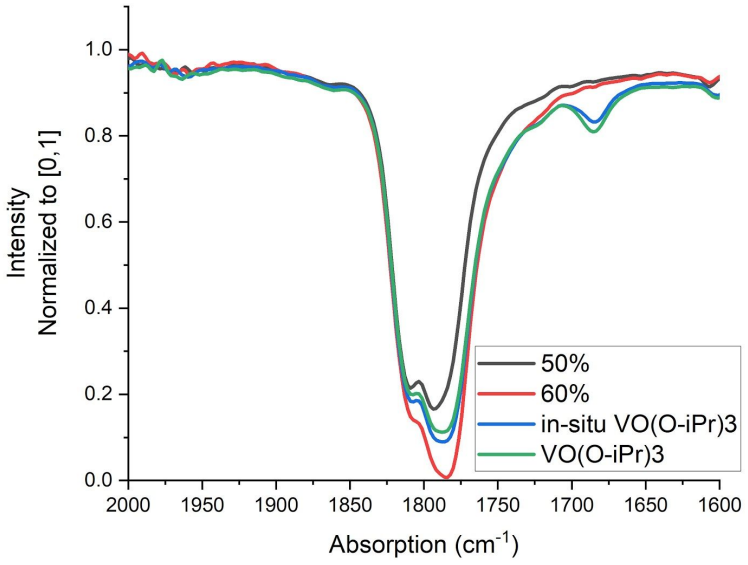


Fig.14 The IR spectra of in-situ $VO(OiPr)_3$, $VO(OiPr)_3$ compared with reference samples.

The high yields from the trials experiments with $VO(O\text{-}iPr)_3$ were very satisfying and it is the best out of all metal precursors that has been tested, therefore $VO(O\text{-}iPr)_3$ was chosen for further research of its catalytic activities under different conditions, and in addition to that, we were interested to find out whether solvent would affect the structure of the complex and leads to affecting the yield of cyclic carbonate.

The solution of the reaction of H_2L with $VO(O\text{-}iPr)_3$ was changed from MeOH to isopropanol. The refluxing and crystallization processes remained the same, as result, dark-colored crystal products were obtained. The products obtained from a MeOH solution were at most 37% yield, and from an isopropanol solution, it reached almost 95% yield. There are two analogous but still different products, in order to analyze and differentiate the characteristics of both products, both products were used as catalysts in coupling reactions and data were collected separately.

In the first phase of experimental data collection, experiments were performed on finding the effects of parameters to experimental results. In all of the parameters, the molar ratio was first tested, by testing samples with 1, 2 and 5 mol% ratio of catalyst to epoxide, result shows that the yields were almost the same (See Fig.15). It can be concluded that the molar ratio has no significant effect on the yield percentage of this experimental work, and thus the rest of the experiments use a 1 mol% ratio consistently.

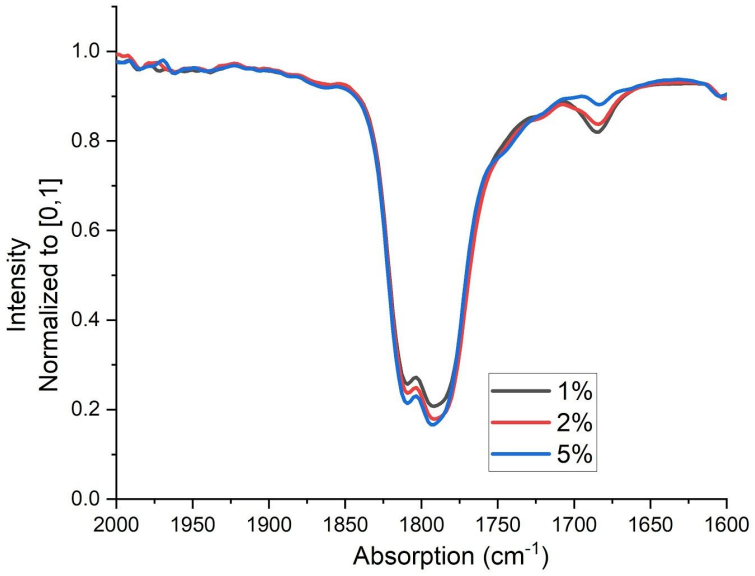


Fig.15 The IR spectra of yields in different molar ratios.

Other parameters were tested with different values as well. The experimental data from these parameters indicates that the longer time, higher temperature and higher pressure will positively affect the yield (see Fig.17). In order to find trends and the best combination of parameters for the highest yields, all possible combinations were performed in the experiments, and data was collected as shown in Table.2 Parameter combinations in coupling reaction at the end of this section.

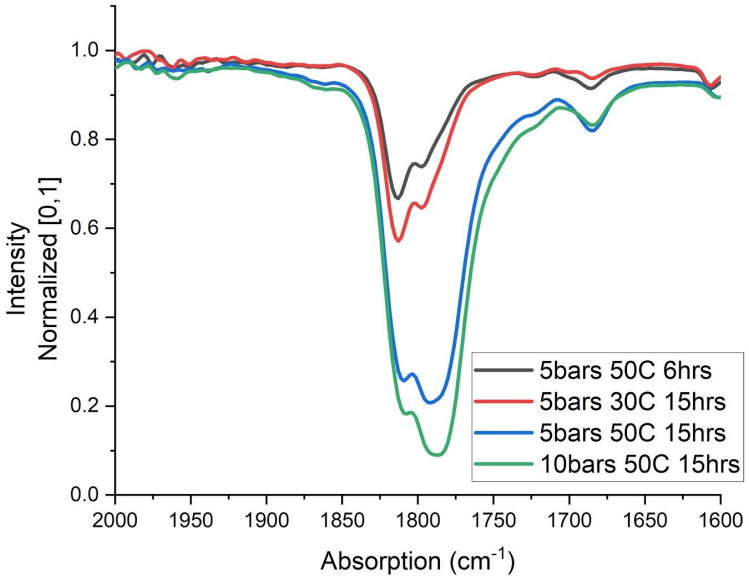


Fig.17 The IR spectra of yields compared in different parameters.

The yields of all samples are documented in Table.3 Cyclic carbonate yields at the end of this section. A total of 30 sample sets, 120 samples, vast majority has shown a yield of 0 - 10%, which most likely is the catalytic effect from the pro-ligand part of the complex. There's 14.2% of the samples shown 0 yield, which could mean the vanadium complex has most likely dissociated, and coupling reaction did not happen under corresponding condition. These two major groups account for 60% of the experiments, the remaining 40% (48 samples) distributed in 18 samples in 10% - 20% and 16 samples in 20% - 30%, 2 samples in 30% - 40%, 9 samples in 40% - 50% and 3 samples in 50% - 60%. If the high yield threshold was set to 40%, only 10% of all samples have shown significant effectiveness under the respective experimental conditions.

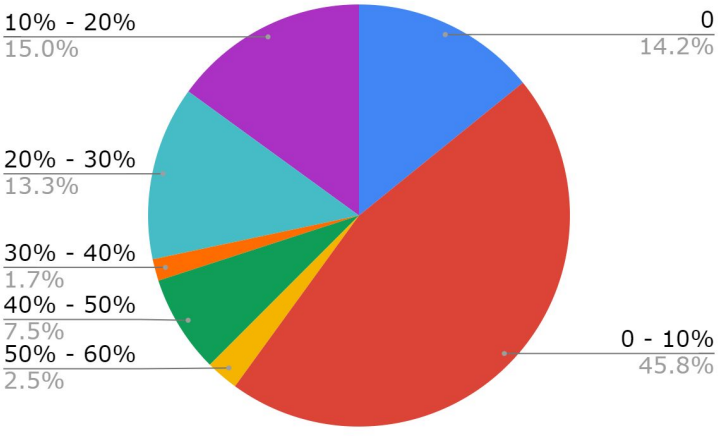


Fig.18 Sample Yield Proportions

The common affecting factor for the high-yield reactions is the higher-valued parameter, this refers to the highest values in each parameter. For example, when the remaining parameters are all at low-value, having a coupling reaction done in the highest value of 10 bars compared with another highest value of 75 ºC condition, the yields could be the same. The affecting factors can be added up to achieve better yields, having one parameter at its highest value certainly has its limitation to boost the catalytic performance, but having multiple parameters at its highest would make the experiment yield at the optimal state.

Catalytic Coupling of Styrene Oxide and CO_2 with Complex V1

At a constant temperature of 25ºC, the yield does not rise linearly with the increase of time. At any time interval, when the pressure is at 10 bars, the yield fluctuates, and the pressure and the yield are exponentially related.

At a constant temperature of 50ºC, the general trend is the same. It is interesting to note that under the low pressure of 1 bar, time plays an important effect. Compared with 3, 9, and 15 hours, the yield of the 21-hour's experiment suddenly increased, and the duration and yield were exponentially related. Under the condition of 5 bars, the yield gradually increases as time increases, forming a linear relationship. Under the condition of 10 bars, the sample with time of 9 hours has the lowest yield. Conversely, the yield of 3 hours and 15 hours was higher than that at 9 hours under the same conditions. It can be concluded that before 9 hours, there was a negative correlation between duration and yield, and after 9 hours, there was a positive correlation.

At a constant temperature of 75ºC, both duration and pressure are directly proportional to yield.

Catalytic Coupling of Cyclohexene Oxide and CO_2 with Complex V1

At a constant temperature of 25ºC, the yield increases exponentially under all pressures with increasing duration, but within this range, the yield is the highest and most stable at 5 bars.

At a constant temperature of 50ºC, all samples have dissociated at a low pressure of 1 bar and no yields. Under the condition of 5 bars, time has no effect on yield, and the sample in the 9 hour's experiment also exhibited no yield. Under the condition of 10 bars, time is negatively correlated with yield at 15 hours, and positively correlated after 15 hours.

At a constant temperature of 75ºC, short-time low pressure and long-time high pressure did not show good results on yields. Under short-time high pressure conditions, the yield is at its best.

Catalytic Coupling of Styrene Oxide and CO_2 with Complex V2

At a constant temperature of 25ºC, time and pressure have no effect on yield.

At a constant temperature of 50ºC, at the state of 1 bar, time has no effect on yield. Under the condition of 5 bars, it is exponentially related, and under the condition of 10 bars it exhibits a faster exponential growth.

At a constant temperature of 75ºC, time and pressure are directly proportional to yield.

Catalytic Coupling of Cyclohexene Oxide and CO_2 with Complex V2

At a constant temperature of 25ºC, 1 bar and 5 bars conditions show that time and yield have an inverse exponential relationship, and 10 bar shows a exponential relationship

At a constant temperature of 50ºC, all samples have dissociated at a low pressure of 1 bar and no yields. Under the condition of 5 bars, the yield was the highest in the 15 hours experiment. There was no yield before 15 hours, and the yield of experiment over 15 hours was reduced. Under the condition of 10 bars, time has an inverse exponential relationship with yield.

At a constant temperature of 75ºC, time and pressure are positively related to yield.

High Yield Samples

By comparing all IR spectra data, the most productive samples were confirmed of **V1SO215010** (complex V1 with styrene oxide with condition of 21 hours, 50ºC, 10 bars), **V2SO155010** (complex V2 with styrene oxide with condition of 15 hours, 50ºC, 10 bars) and **V2SO215010** (complex V2 with styrene oxide with condition of 21 hours, 50ºC, 10 bars). All yielded in the range of 50% to 60%.

Fig.19 shows that all three samples are of almost identical yield to each other, given that two samples of **V2SO** are 6 hours difference, it can be that **V2SO155010** has already reached its catalytic limit at 15 hours of reaction, hence the result of **V2SO215010** may not be very accurate. The two high yielding samples, both involving styrene oxide, compared to Table.3 with lower tier yields in the range of 40% - 50% and 30% - 40%, and Table.4 where it shows the product status, it can be concluded that the vanadium complexes in this thesis work, has a better catalytic performances with styrene oxide, it produces high yields and the products presents in liquid state.

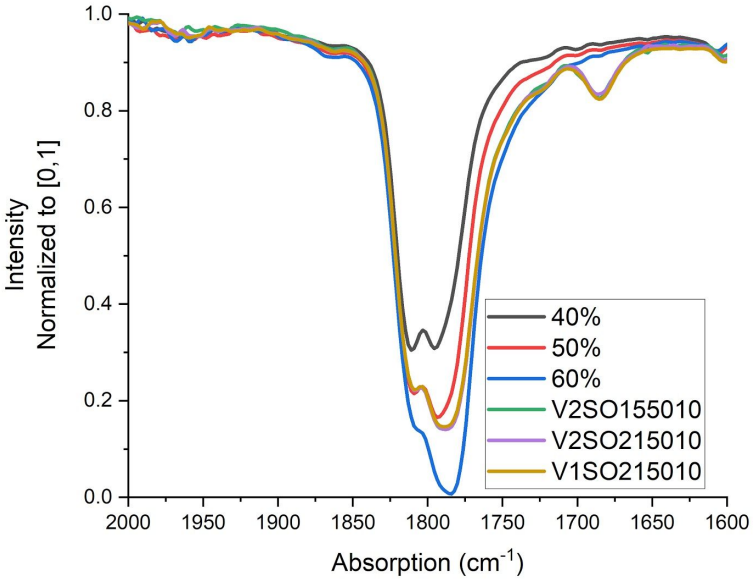


Fig.19 The IR spectra of three highest yielding samples compared with reference samples.

3.4 TON, TOF & Conversion rate

Turnover number TON in organometallic catalysis, it refers to the number of moles of substrate that a mole of a catalyst can convert before becoming inactivated. TOF is the turnover frequency, that is, turnover per unit time. The mole of product is estimated by ratio with proton numbers of epoxide and cyclic carbonate from the NMR spectra, with such ratio, conversion rate for the most reactive samples are also presented in the table below. Reference NMR in supplementary materials.

Table.6 TON, TOF and conversion rates of high yielding samples

Sample (yield)	Mole of Product (mmol)	Mole of Catalyst (mmol)	TON	TOF (h^{-1})	Conversion (%)
V1SO215010 (50%-60%)	2.74	0.1	27.4	2.74	72.61
V2SO155010 (50%-60%)	2.37	0.1	23.7	2.37	76.28
V2SO215010 (50%-60%)	2.61	0.1	26.1	2.61	74.09
V1SO21505 (40%-50%)	3.26	0.1	32.6	6.52	67.45
V2SO21505 (40%-50%)	3.71	0.1	37.1	3.71	62.92
V1SO155010 (40%-50%)	2.92	0.1	29.2	2.92	70.83
V1SO97510 (30%-40%)	3.59	0.1	35.9	3.59	64.08
V1SO15505 (20%-30%)	3.43	0.1	34.3	6.86	65.69

3.5 Characterizations

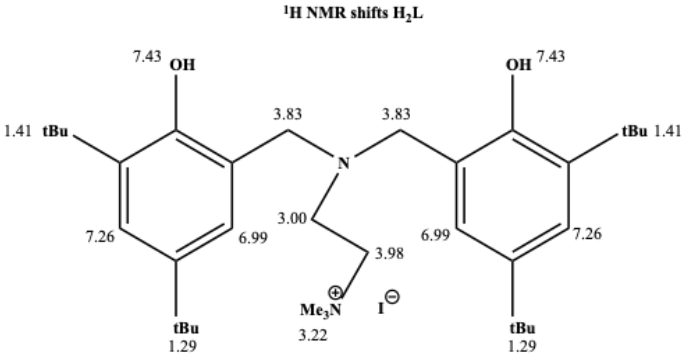


Fig.20 Numbering scheme of H_2L.

H_2L: IR(cm^{-1}) 2954s, 1593w, 1473s, 1444w, 1415m, 1390m, 1361s, 1332m, 1292m, 1247m, 1217s, 1199s, 1157m, 1126m, 1087w, 1014m, 983w, 970w, 946w, 921m, 887s, 821m, 802m, 759w, 725m, 680w, 649w, 605w, 580w, 511m. **^{1}H NMR (300MHz, $CDCl_3$):** δ 7.43 (s, 2H), 7.26 (d, *J* = 2.2 Hz, 2H), 6.99 (d, *J* = 2.1 Hz, 2H), 3.98 (t, *J* = 6.3 Hz, 2H), 3.83 (s, 4H), 3.22 (s, 9H), 3.00 (t, *J* = 6.2 Hz, 2H), 1.41 (s, 18H), 1.29 (s, 18H).

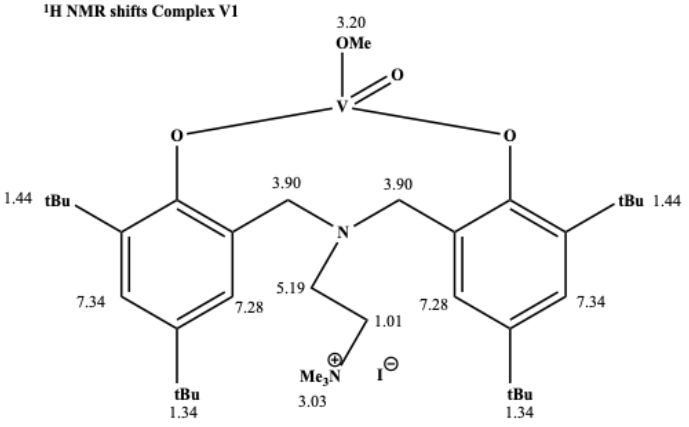


Fig.21 Numbering scheme of complex V1.

V1: IR(cm^{-1}) 2954w, 1438w, 1236m, 1168w, 1054m, 989w, 948w(V=O), 914w, 852m, 806w, 757m, 595s, 549w, 476w, 368w. **^{1}H NMR (300MHz, $CDCl_3$):** δ 7.34 (s, 2H), 7.28 (d, *J = 8.2 Hz*, 2H), 5.19(s, 2H), 3.90 (m, 4H), 3.20 (s, 3H), 3.03 (s, 9H), 1.49 - 1.41 (m, 18H), 1.34 (s, 18H), 1.11 - 0.96 (m, 2H). The exact mass for **[V1 - I]**$^+$ is 635.40 (Mass of the product minus mass of iodide ion 762.31 - 126.91 = 635.40). Other mass values (636.40, 637.39, 638,39) could be formulated with vanadium isotopes and/or carbon isotopes. **V1** has a λ_{max} value at 284.98nm, signal peaks at 230.01 nm and 354.99 nm shown in **UV-vis.**

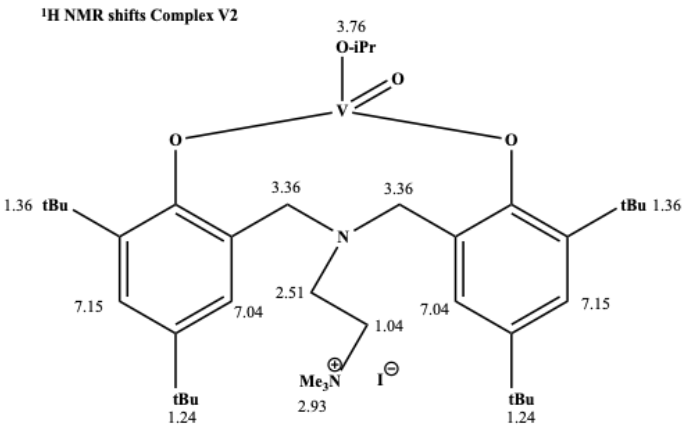


Fig.22 Numbering scheme of complex V2.

V2: IR(cm^{-1}) 2954w, 1438w, 1359w, 1234m, 1201w, 1166w, 1130w, 1109w, 985w, 948w(V=O), 914w, 842s, 808w, 759m, 696w, 646s, 597, 582, 478m, 364w. **^{1}H NMR (300MHz, DMSO):** δ 7.15 (d, *J = 2.2 Hz*, 2H), 7.04 (d, *J = 2.1 Hz*, 2H), 3.79 - 3.74 (m, 6H), 3.36 (s, 48H), 2.93 (s, 9H), 2.51 (m, 14H), 1.36 (s, 18H), 1.24 (s, 18H), 1.04 (d, *J = 6.1 Hz*, 18H). The exact mass for **V2** is 790.34, but there is none showing from the MS. While a mass number of 636.40 shows with a major intensity, which may possibly be a different form of **V1** with isotopes from either vanadium and/or carbon. Other mass values (635.40, 635.71, 637.40, 638.39) could also be other forms of **V1** with isotopes. **V2** has a λ_{max} value at 284.98 nm, signal peaks at 244.99 nm and 360 nm shown in **UV-vis.**

Table.7 Molar absorption coefficients at $\varepsilon_{284.98}$

Concentration	Complex V1 $\varepsilon_{284.98}$	Complex V2 $\varepsilon_{284.98}$
2.57×10^{-4} M	15804 M^{-1} cm^{-1}	16513 M^{-1} cm^{-1}
1.28×10^{-4} M	25585 M^{-1} cm^{-1}	15161 M^{-1} cm^{-1}
2.57×10^{-5} M	22910 M^{-1} cm^{-1}	16872 M^{-1} cm^{-1}
1.28×10^{-5} M	21095 M^{-1} cm^{-1}	13760 M^{-1} cm^{-1}
2.57×10^{-6} M	46809 M^{-1} cm^{-1}	3280 M^{-1} cm^{-1}

3.6 Reference Samples

A total of 30 mmol (10 mmol + 20 mmol) or 3.43 ml of styrene oxide was used for coupling reaction to produce styrene carbonate, experimented twice, after washing, recrystallization and isolation, a total of 1.52 mmol or 0.2495 g of styrene carbonate was collected, with poor yield of 5.1%.

A series of reference samples were made by mixing styrene carbonate and styrene oxide in different ratios. The ratio increases by every 10%, starting from 0 to 90%, a total of 10 samples were made. Each reference sample was measured with IR spectra, and the absorption maxima at 1800 cm^{-1} was selected to compare the intensities with other samples. Details of the composition of each reference sample are recorded in Table.5 Reference Sample Composition.

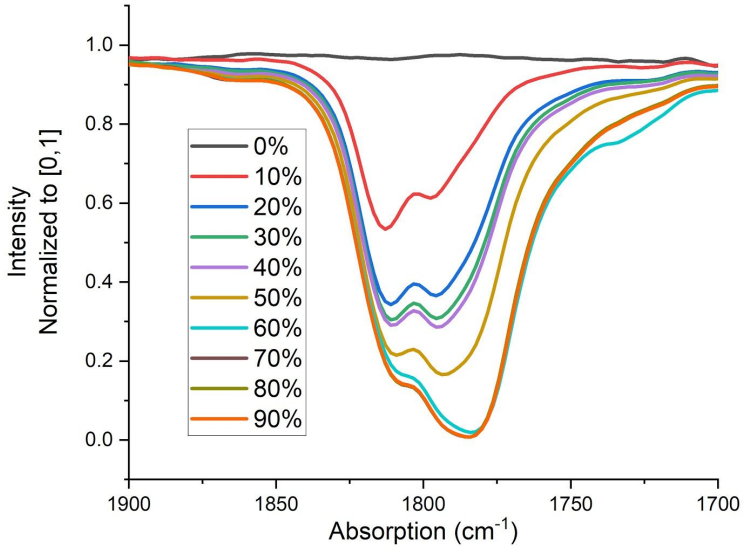


Fig.23 The IR spectra of the styrene carbonate/styrene epoxide mixtures in different compositions.

Fig.23 shows the IR spectra of styrene carbonate/styrene epoxide mixtures in an increasing order. The reference samples with 70%, 80% and 90% styrene carbonate might have very little differences at the absorption peak 1800 cm^{-1}, which resulted in overlapping in the figure.

Table.2 Parameter combinations in coupling reaction.

Entry	Time (Hours)	Temperature (°C)	Pressure (Bar)
#1	3	25	1
#2	3	25	5
#3	3	25	10
#4	9	25	1
#5	9	25	5
#6	9	25	10
#7	15	25	1
#8	15	25	5
#9	15	25	10
#10	21	25	1
#11	21	25	5
#12	21	25	10
#13	3	50	1
#14	3	50	5
#15	3	50	10
#16	9	50	1
#17	9	50	5
#18	9	50	10
#19	15	50	1
#20	15	50	5
#21	15	50	10
#22	21	50	1
#23	21	50	5
#24	21	50	10
#25	3	75	1
#26	3	75	5
#27	3	75	10
#28	9	75	1
#29	9	75	5
#30	9	75	10

Table.3 Cyclic carbonate yields.

Entry	V1SO	V1CHO	V2SO	V2CHO
#1	0 - 10%	0	0 - 10%	20% - 30%
#2	0 - 10%	10% - 20%	0 - 10%	10% - 20%
#3	40% - 50%	0 - 10%	0 - 10%	0 - 10%
#4	0 - 10%	0	0 - 10%	20% - 30%
#5	0 - 10%	10% - 20%	0 - 10%	10% - 20%
#6	40% - 50%	0 - 10%	0 - 10%	0 - 10%
#7	0 - 10%	0	0 - 10%	20% - 30%
#8	0 - 10%	10% - 20%	0 - 10%	10% - 20%
#9	40% - 50%	0 - 10%	0 - 10%	0 - 10%
#10	0 - 10%	20% - 30%	0 - 10%	0
#11	0 - 10%	20% - 30%	0 - 10%	0 - 10%
#12	0 - 10%	10% - 20%	0 - 10%	10% - 20%
#13	0 - 10%	0	0 - 10%	0
#14	10% - 20%	20% - 30%	0 - 10%	0
#15	10% - 20%	20% - 30%	0 - 10%	20% - 30%
#16	0 - 10%	0	0 - 10%	0
#17	10% - 20%	0	10% - 20%	0
#18	0 - 10%	20% - 30%	40% - 50%	10% - 20%
#19	0 - 10%	0	0 - 10%	0
#20	20% - 30%	30% - 40%	40% - 50%	20% - 30%
#21	40% - 50%	0 - 10%	50% - 60%	0 - 10%
#22	30% - 40%	0	0 - 10%	0
#23	40% - 50%	10% - 20%	40% - 50%	0 - 10%
#24	50% - 60%	10% - 20%	50% - 60%	0 - 10%
#25	0 - 10%	0	0 - 10%	0
#26	0 - 10%	10% - 20%	10% - 20%	0 - 10%
#27	10% - 20%	20% - 30%	10% - 20%	0 - 10%
#28	0 - 10%	0 - 10%	0 - 10%	0 - 10%
#29	20% - 30%	0 - 10%	20% - 30%	0 - 10%
#30	30% - 40%	0 - 10%	40% - 50%	0 - 10%

Table.4 Samples wet and dry conditions.

Entry	V1SO	V1CHO	V2SO	V2CHO
#1	Liquid	Dry	Liquid	Semi-dry
#2	Dry	Dry	Dry	Dry
#3	Liquid	Dry	Liquid	Dry
#4	Liquid	Dry	Liquid	Liquid
#5	Semi-dry	Dry	Semi-dry	Dry
#6	Dry	Dry	Dry	Dry
#7	Liquid	Liquid	Liquid	Liquid
#8	Liquid	Semi-dry	Liquid	Liquid
#9	Liquid	Dry	Semi-dry	Dry
#10	Dry	Dry	Dry	Dry
#11	Liquid	Liquid	Liquid	Semi-dry
#12	Liquid	Dry	Liquid	Dry
#13	Liquid	Dry	Liquid	Liquid
#14	Dry	Dry	Dry	Dry
#15	Semi-dry	Liquid	Liquid	Semi-dry
#16	Liquid	Liquid	Liquid	Liquid
#17	Liquid	Dry	Liquid	Dry
#18	Liquid	Liquid	Liquid	Liquid
#19	Liquid	Liquid	Liquid	Liquid
#20	Liquid	Liquid	Dry	Semi-dry
#21	Liquid	Dry	Liquid	Liquid
#22	Liquid	Liquid	Liquid	Semi-dry
#23	Liquid	Liquid	Liquid	Liquid
#24	Liquid	Semi-dry	Liquid	Liquid
#25	Liquid	Semi-dry	Liquid	Liquid
#26	Liquid	Dry	Liquid	Dry
#27	Liquid	Dry	Liquid	Dry
#28	Semi-dry	Dry	Semi-dry	Dry
#29	Semi-dry	Dry	Semi-dry	Dry
#30	Liquid	Liquid	Liquid	Liquid

Table.5 Reference Sample Composition.

Entry	Styrene Carbonate		Styrene oxide	
#1	0.02mmol	3.2832mg	0.18mmol	20.5974μl
#2	0.04mmol	6.5664mg	0.16mmol	18.3088μl
#3	0.06mmol	9.8496mg	0.14mmol	16.0202μl
#4	0.08mmol	13.1328mg	0.12mmol	13.7316μl
#5	0.10mmol	16.416mg	0.10mmol	11.443μl
#6	0.12mmol	19.6992mg	0.08mmol	9.1544μl
#7	0.14mmol	22.9824mg	0.06mmol	6.8658μl
#8	0.16mmol	26.2656mg	0.04mmol	4.5772μl
#9	0.18mmol	29.5488mg	0.02mmol	2.2886μl
#10	0.20mmol	32.832mg	0	0
TOTAL	1.10mmol	180.576mg	0.90mmol	102.98μl

4. Conclusion

Complex **V1** and **V2** were synthesized in two different solvents and were expected to be different by only the group coordinated to the vanadium center, **V1** with -OMe and **V2** with -O-iPr. The two complexes have shown many similarities in the IR spectra, most peaks are matching with each other except in the range of 900-1200 cm^{-1}. Under UV-vis, the λ_{max} values were of the same 284.98nm, it is truly difficult to identify each other. Mass spectra have shown evidence on the similarity of complexes, as the exact masses are very close to each other, but the distribution of isotopes are different.

In NMR spectra, it has shown the most significant structural differences of both complexes. The bridging position (3.36ppm) and both positions on the sidearm (2.51ppm, 1.04ppm) at **V2** has rather high intensities of hydrogen atoms compared with **V1**. It may be that the complex **V2** is a polymer or a dimer, but it was not synthesized in the correct method.

TOF values of the listed high yielding catalytic reactions in Table.6 are relatively lower than those published value with Williams et al., bimetallic Co(II) (TOF = 172 h^{-1}) and mixed metallic Co(II)/Co(III) (TOF = 159 h^{-1}), which were active with CHO. Complex **V1** can be assumed as effective with styrene oxide, as most of the high yielding samples are done with V1 and styrene oxide. Further research needs to be done in order to improve yield and performances.

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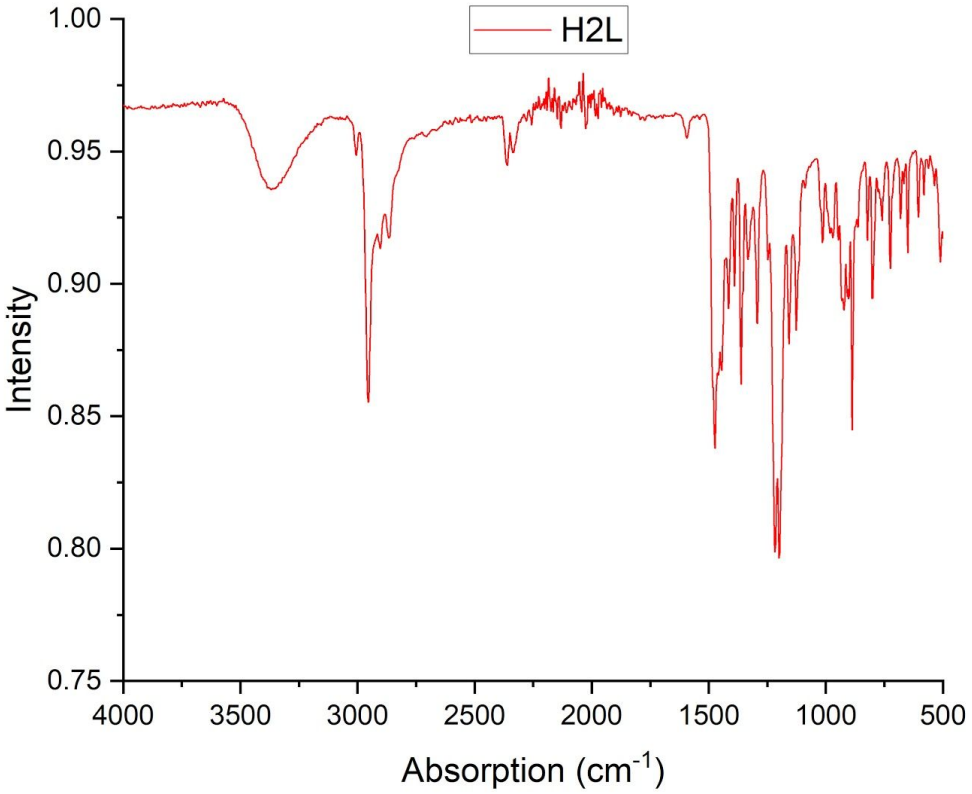
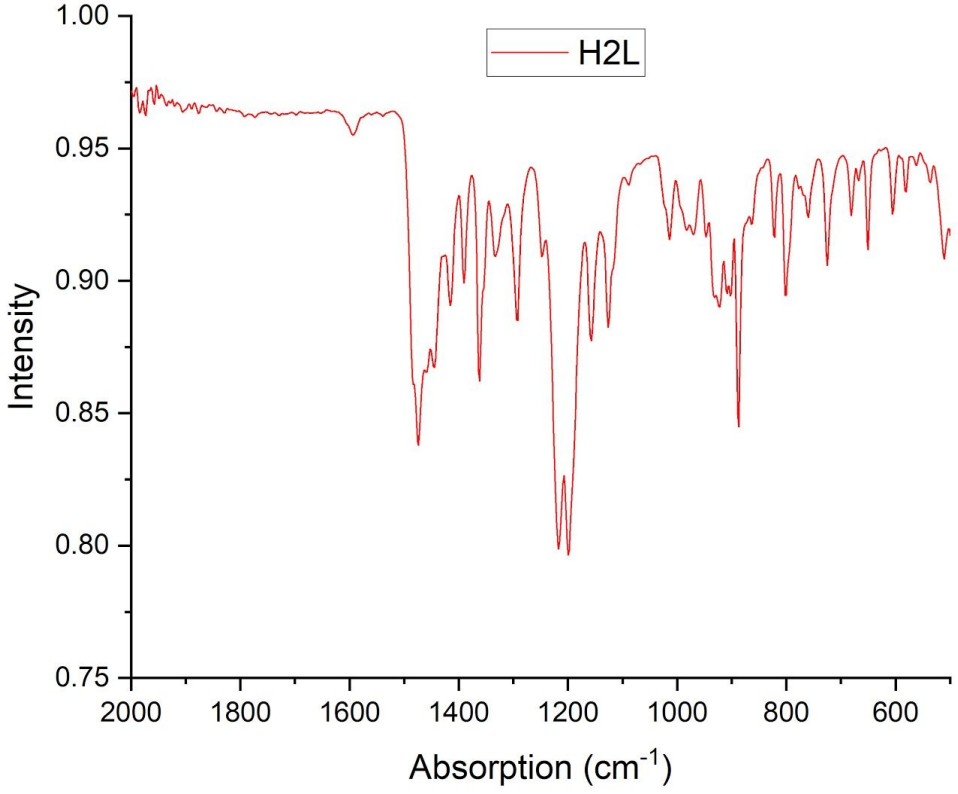
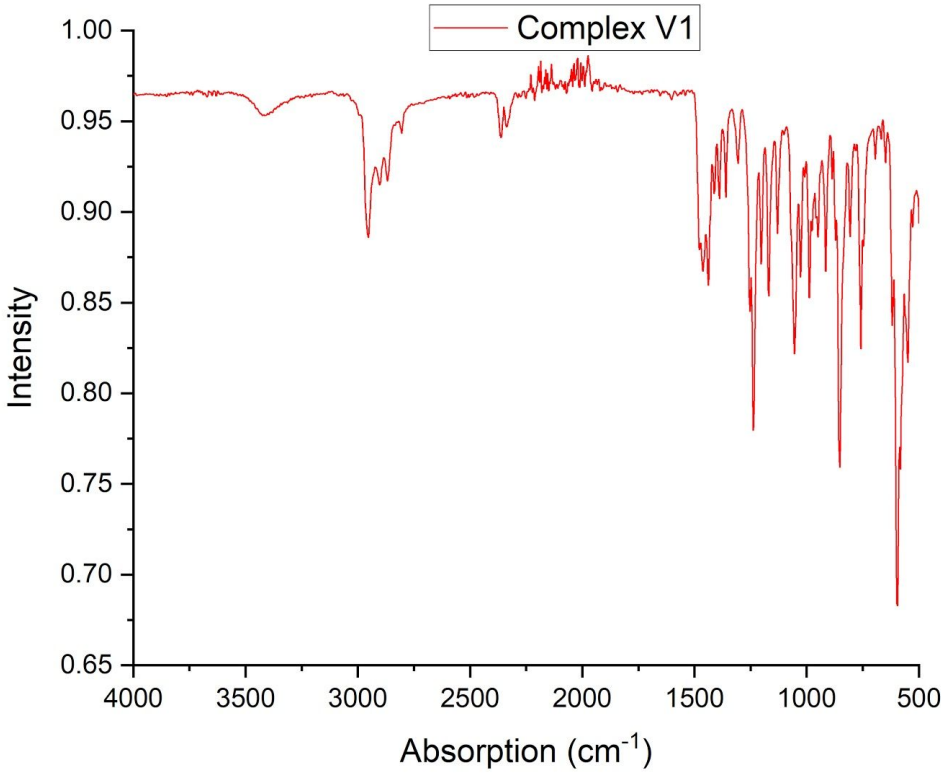
Supplementary Materials

IR Spectra



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0.90
0.85
0.80
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0.70
0.65
Intensity
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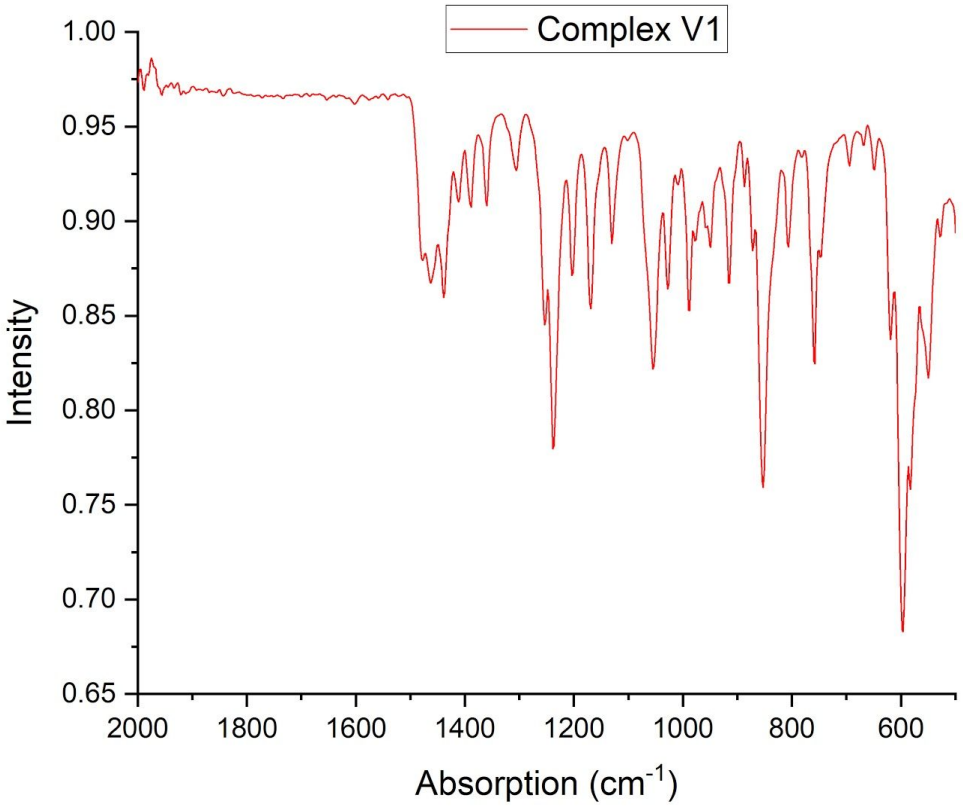
3500
3000
2500
2000
1500
1000
500
Absorption (cm-1)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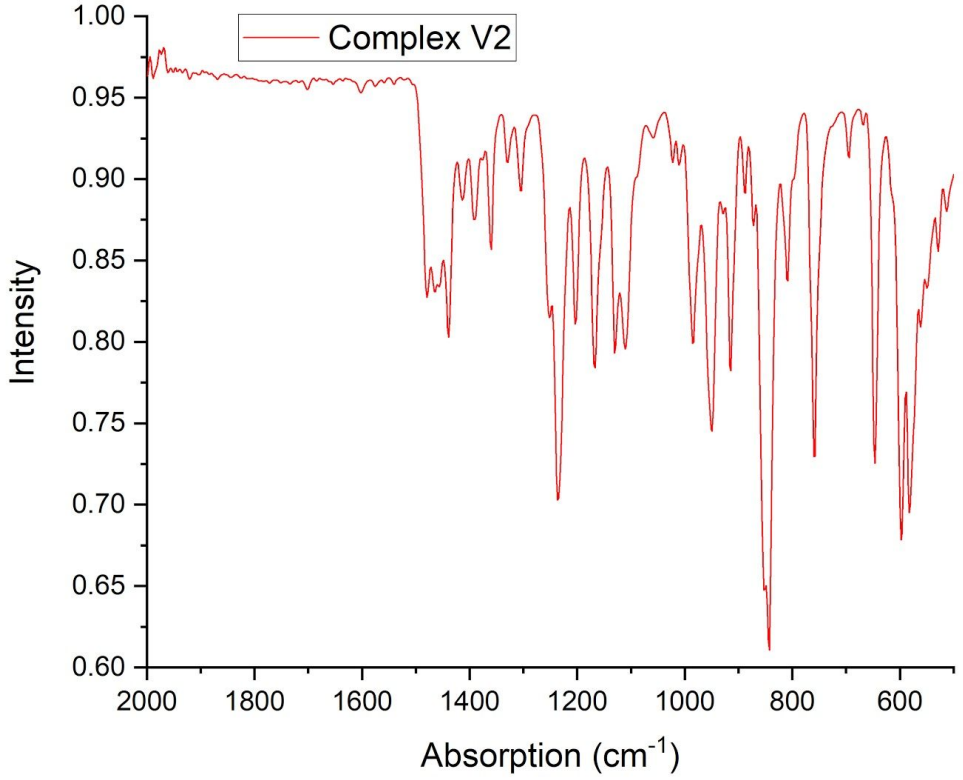
Absorption (cm-1)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1600
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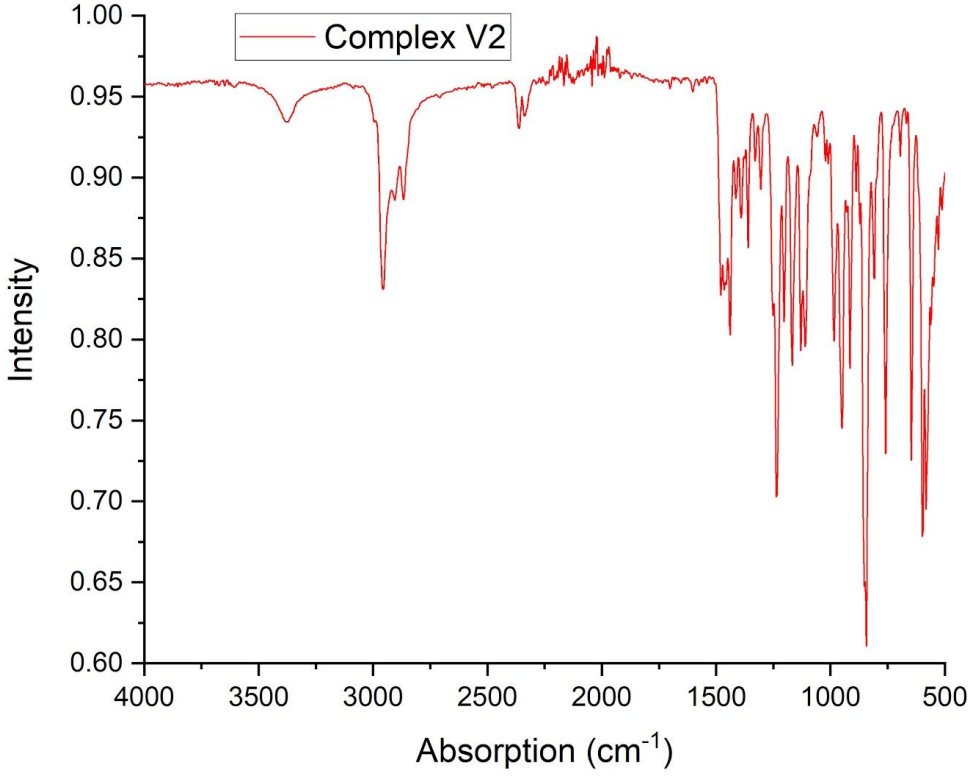
800
600
Absorption (cm-1)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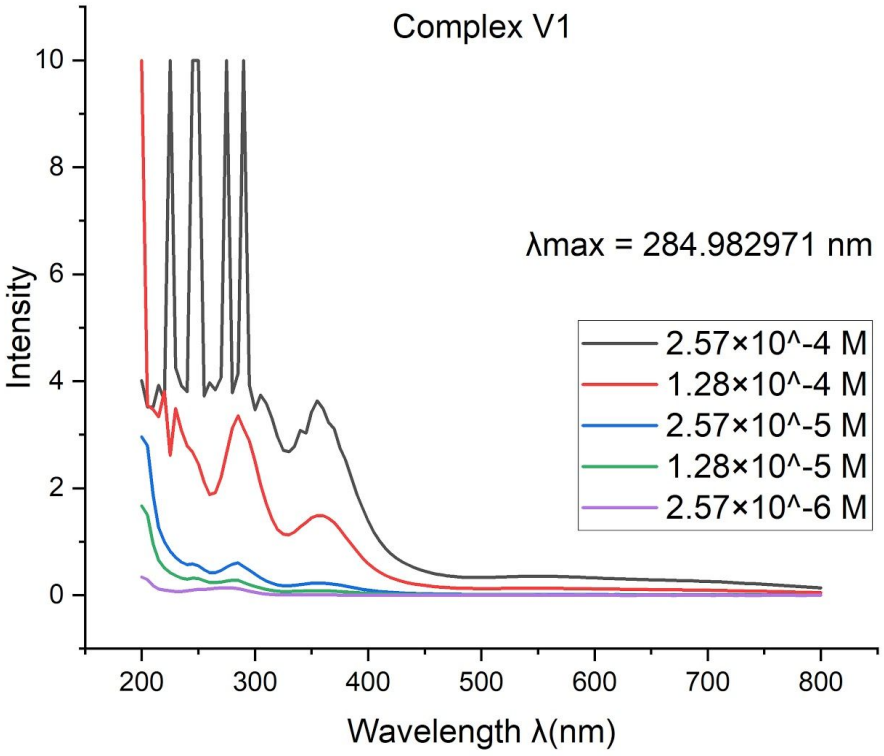
1500
1000
500
Absorption (cm-1)

UV-VIS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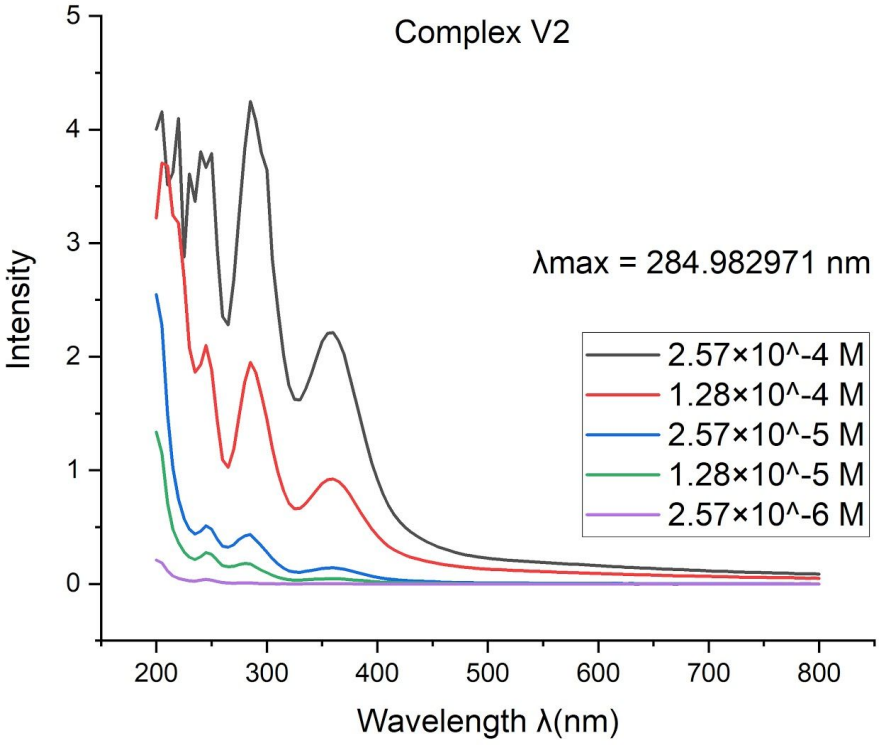
2.57×10^-4 M
1.28×10^-4 M
2.57×10^-5 M
1.28×10^-5 M
2.57×10^-6 M
Intensity
Wavelength λ(nm)
0
2
4
6
8
10
200
300
400
500
600
700
800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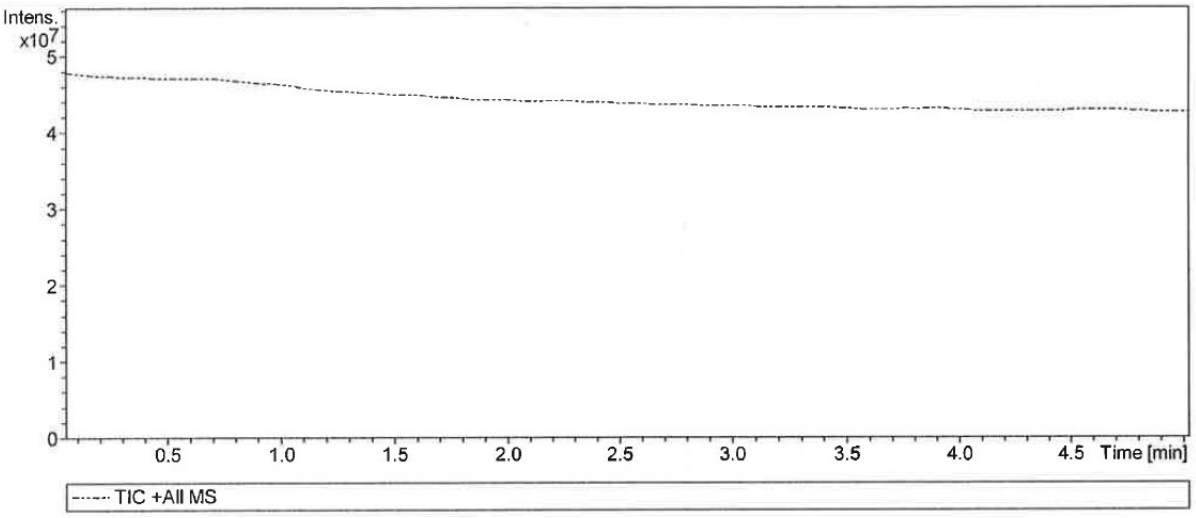
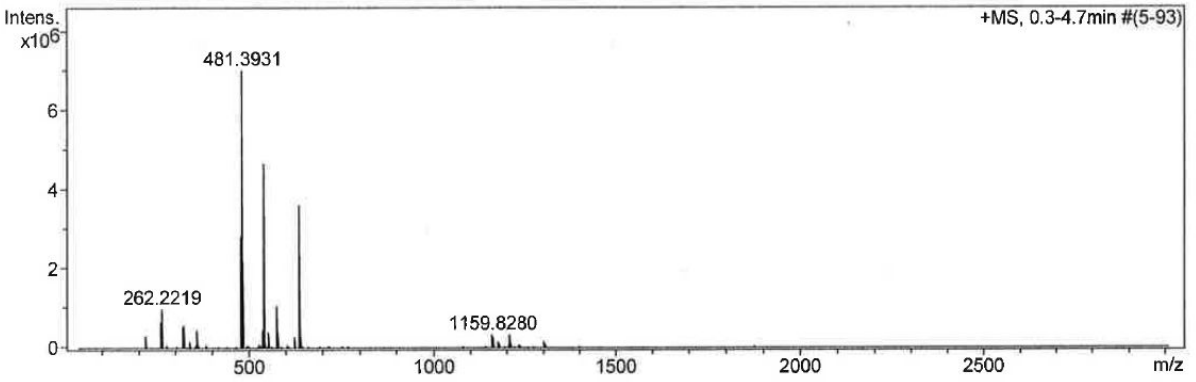
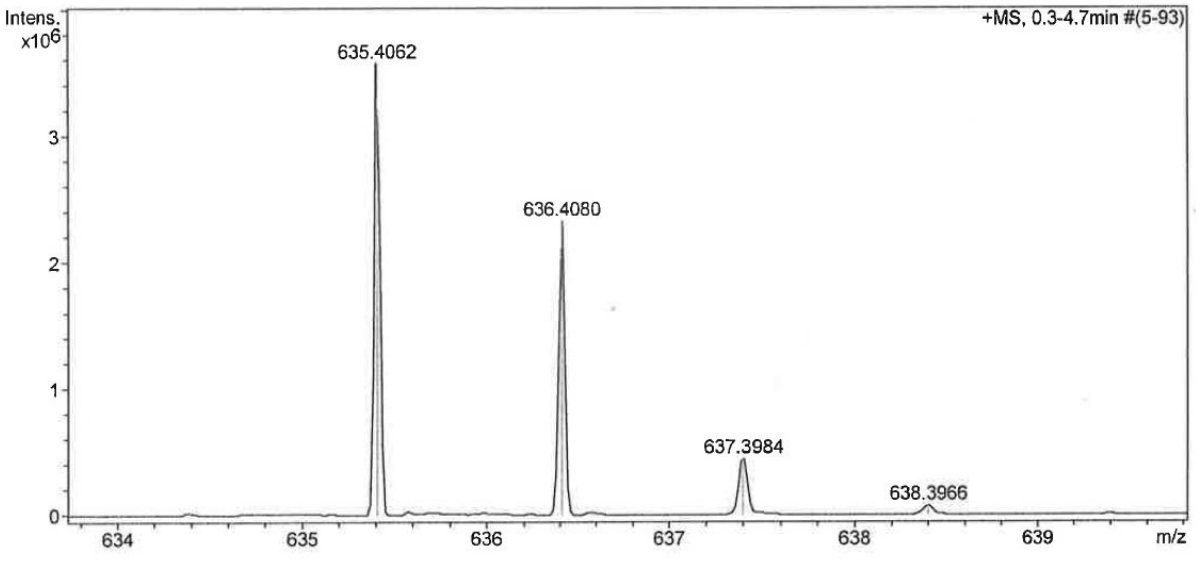
λmax = 284.982971 nm
2.57×10^-4 M
1.28×10^-4 M
2.57×10^-5 M
1.28×10^-5 M
2.57×10^-6 M
Intensity
Wavelength λ(nm)
0
1
2
3
4
5
200
300
400
500
600
700
800

Mass spectroscopy

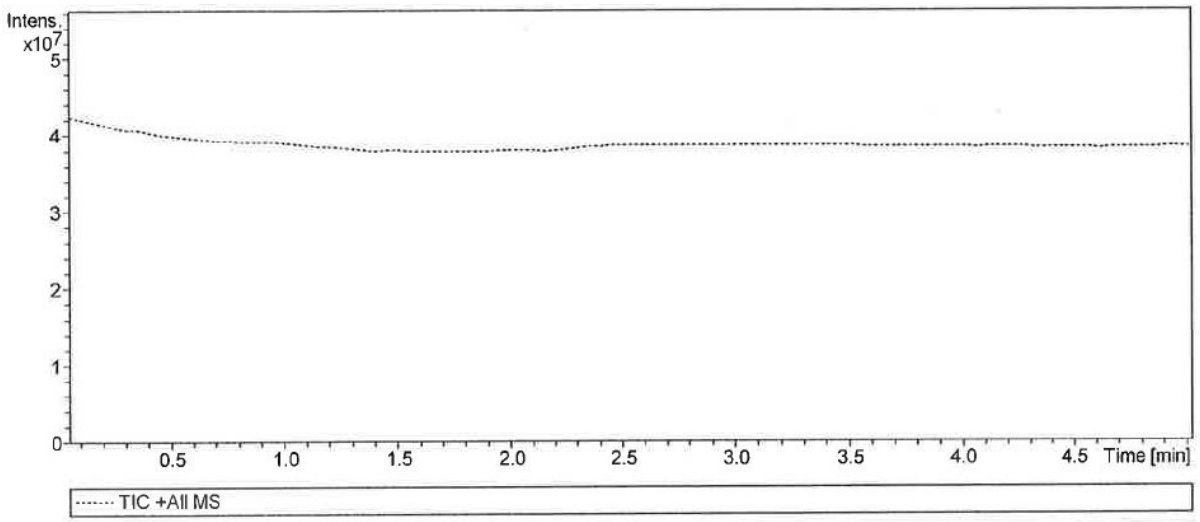
MZ 40-3000 sensitive POS.m (Complex V1)

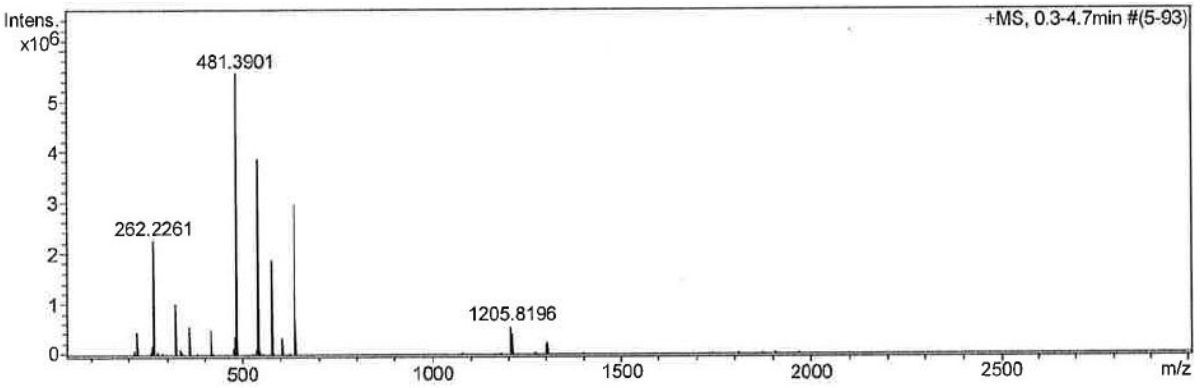


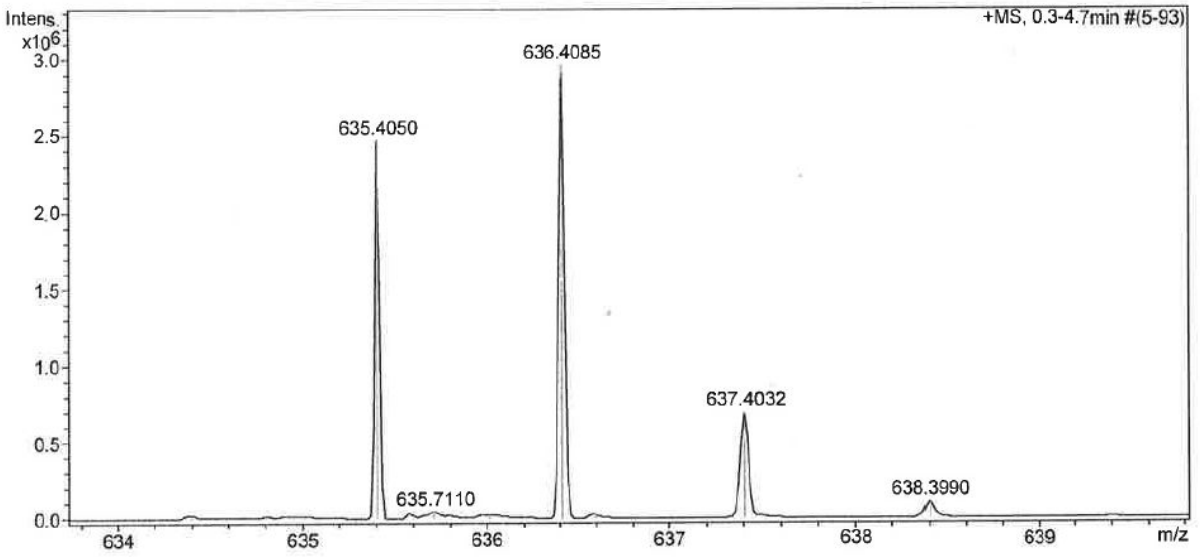




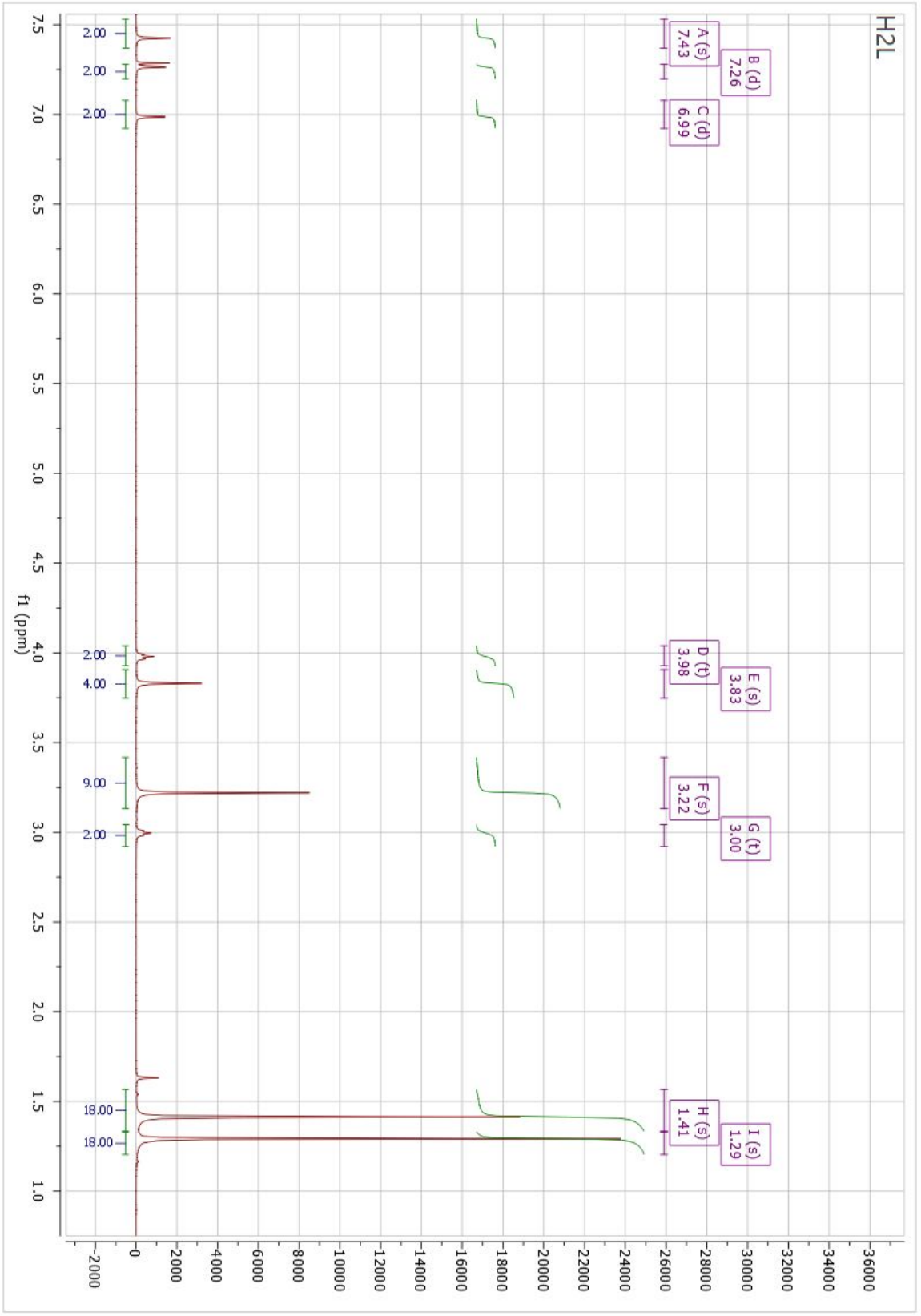
MZ 40-3000 sensitive POS.m (Complex V2)

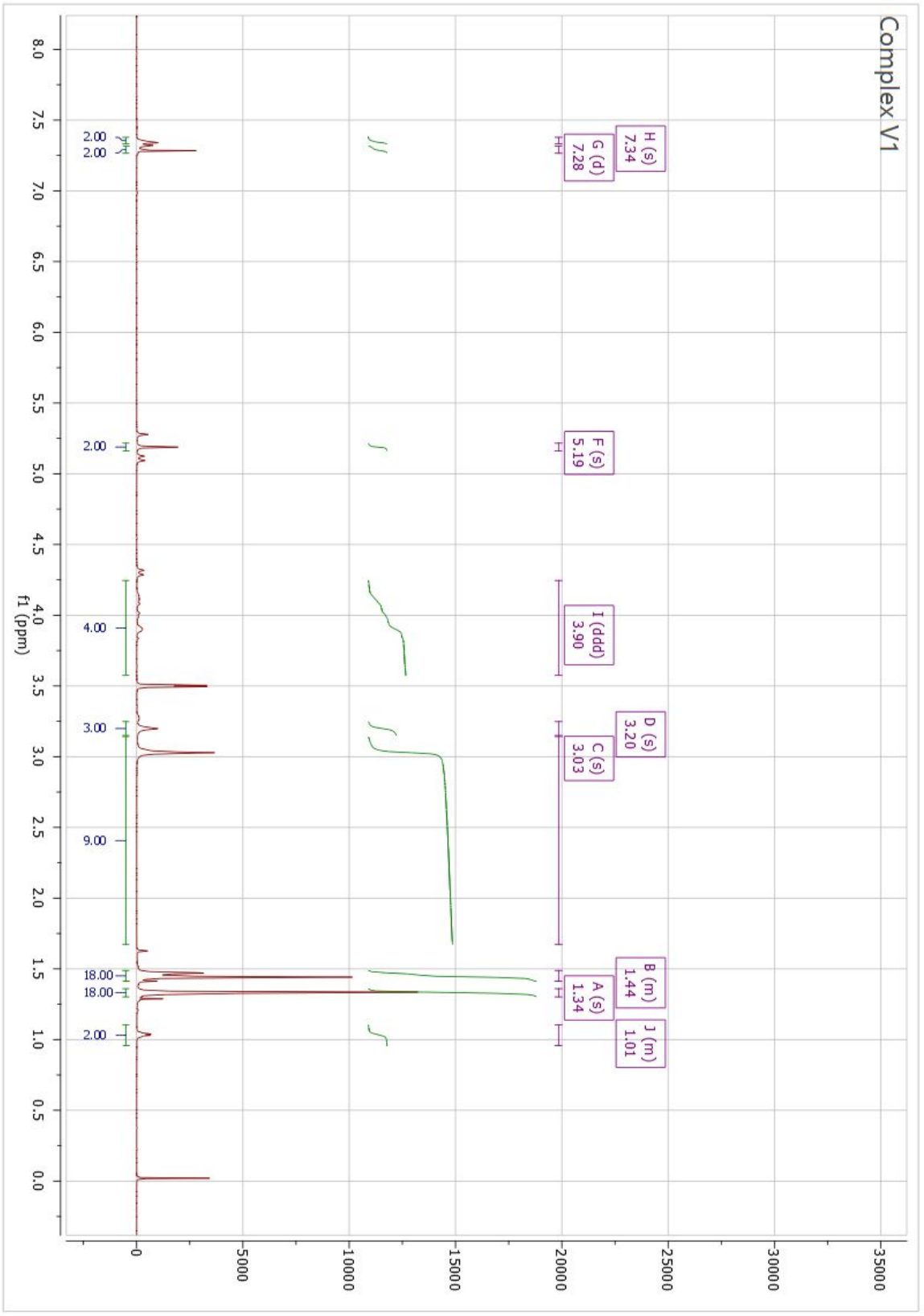


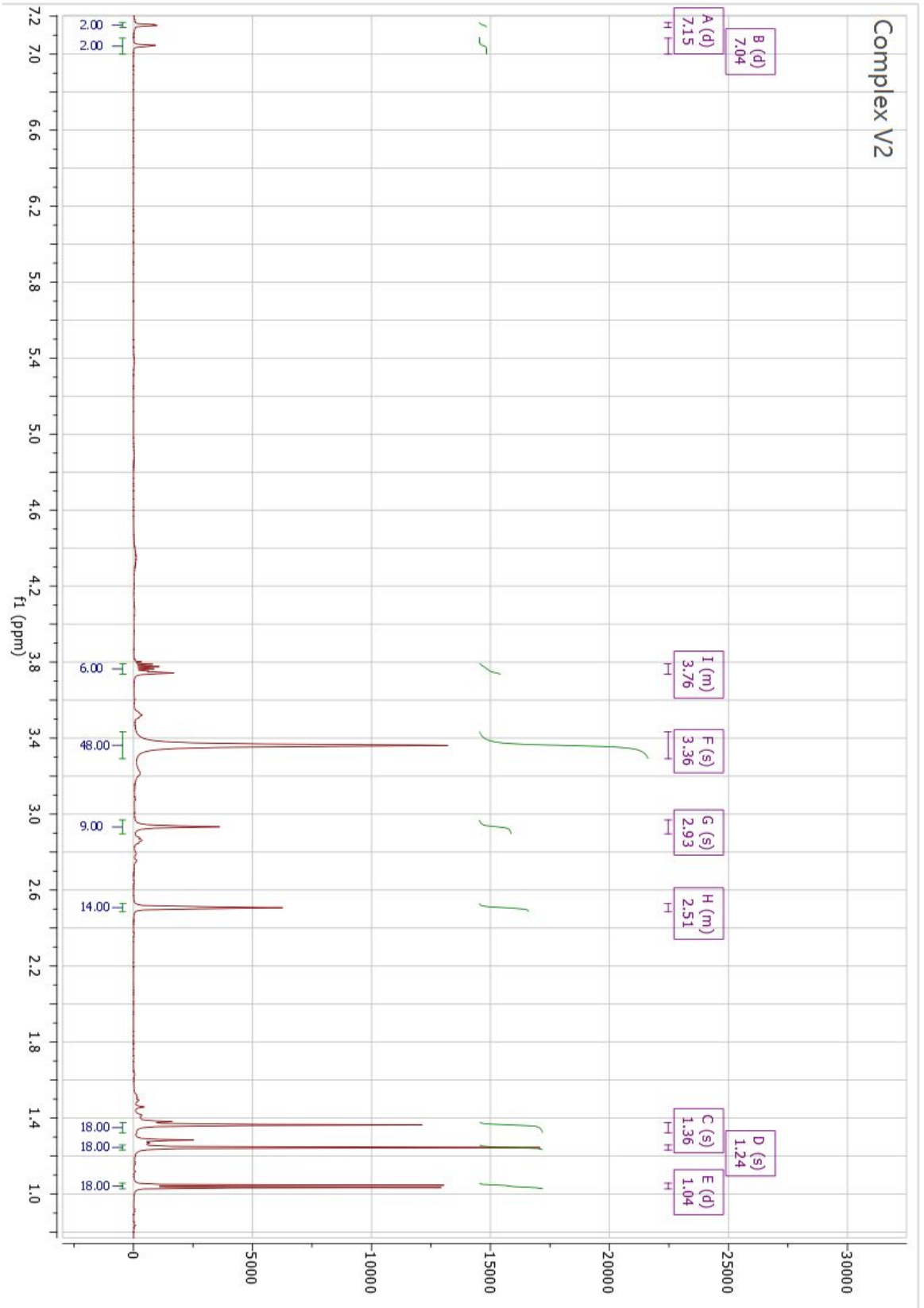




NMR


H2L
A (s) 7.43
B (d) 7.26
C (d) 6.99
D (t) 3.98
E (s) 3.83
F (s) 3.22
G (t) 3.00
H (s) 1.41
I (s) 1.29
2.00
2.00
2.00
2.00
4.00
9.00
2.00
18.00
18.00
f1 (ppm)


Complex V1
H (s)
7.34
G (d)
7.28
F (s)
5.19
I (ddd)
3.90
D (s)
3.20
C (s)
3.03
B (m)
1.44
A (s)
1.34
J (m)
1.01
2.00
2.00
2.00
4.00
3.00
9.00
18.00
18.00
2.00
f1 (ppm)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A (d)
7.15
B (d)
7.04
I (m)
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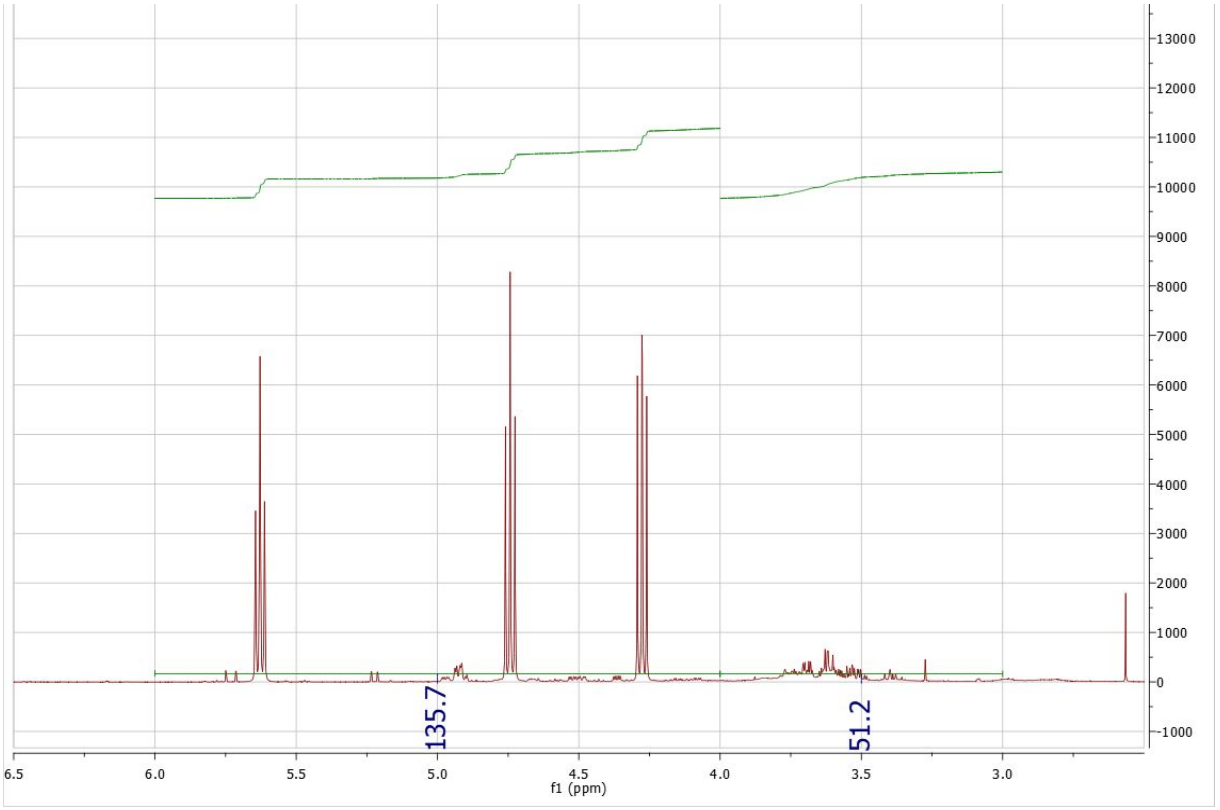
F (s)
3.36
G (s)
2.93
H (m)
2.51
C (s)
1.36
D (s)
1.24
E (d)
1.04
2.00
2.00
6.00
48.00
9.00
14.00
18.00
18.00
18.00
f1 (ppm)

Sample V1SO215010, 1H, $CDCL_3$, 298K, 500MHz



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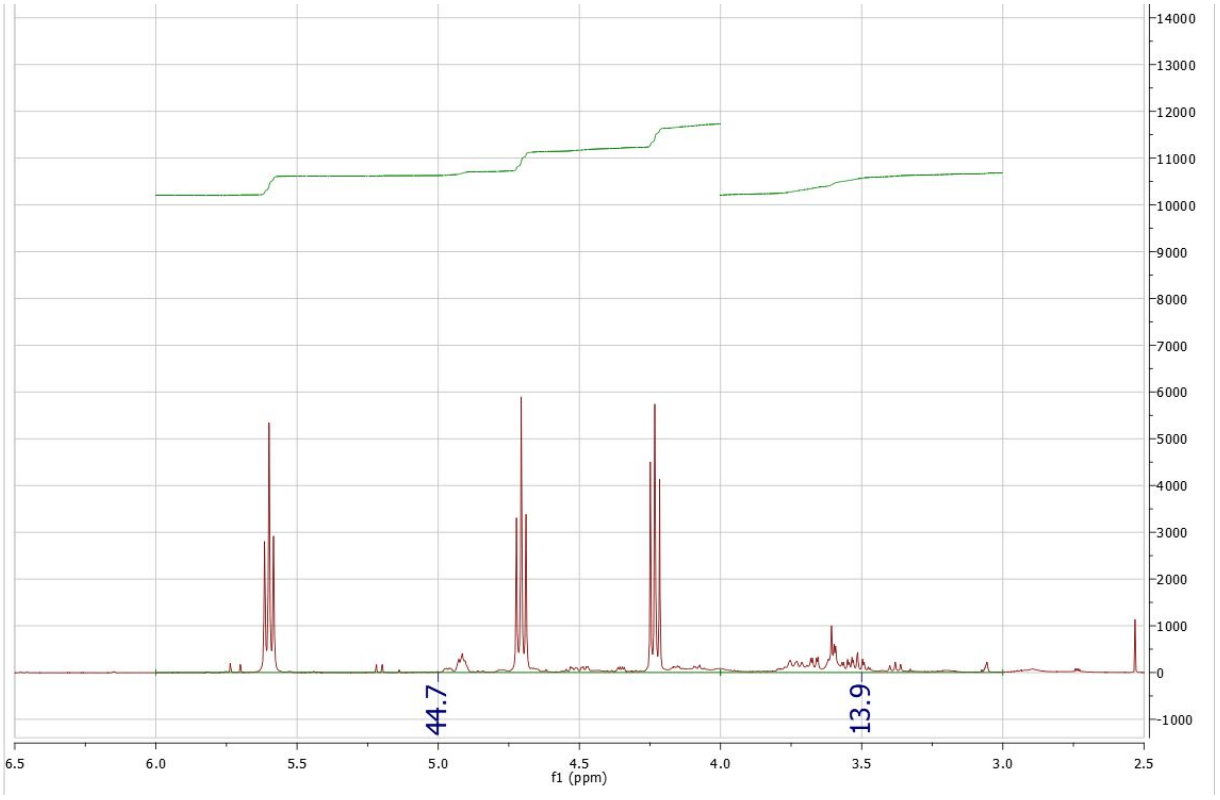

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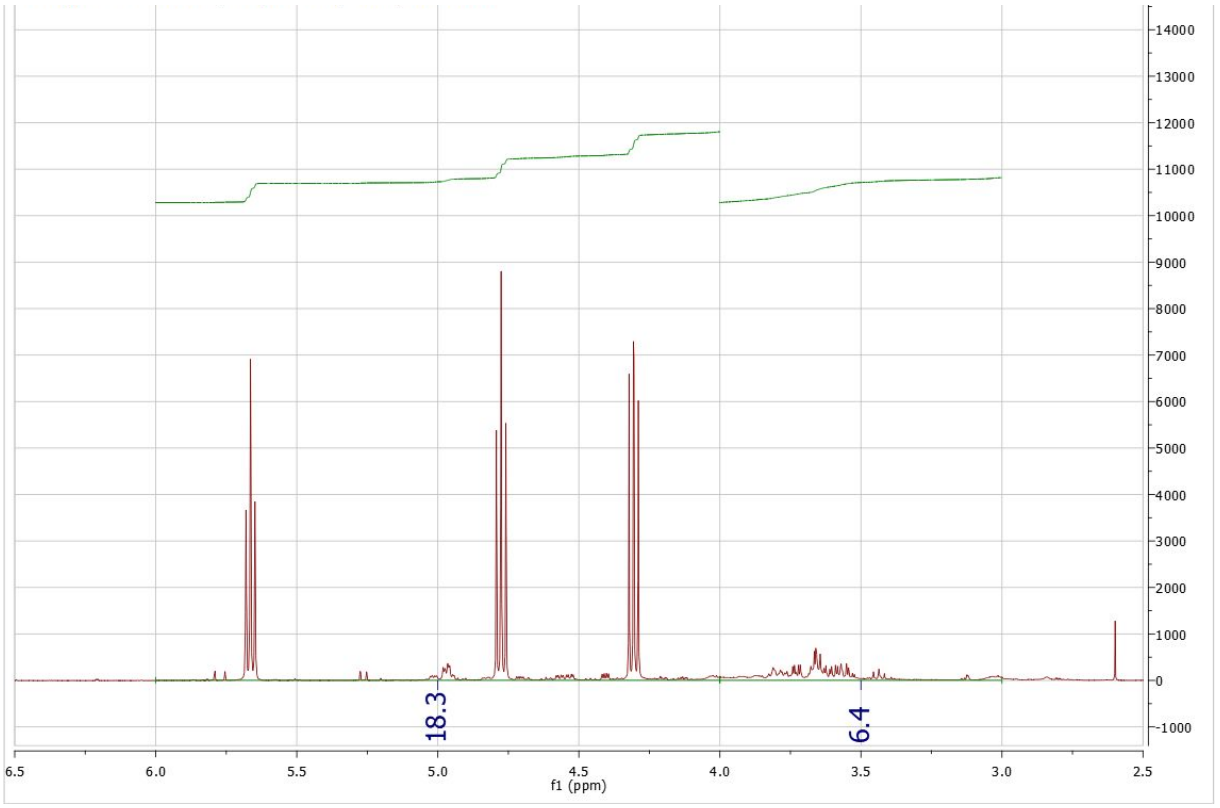

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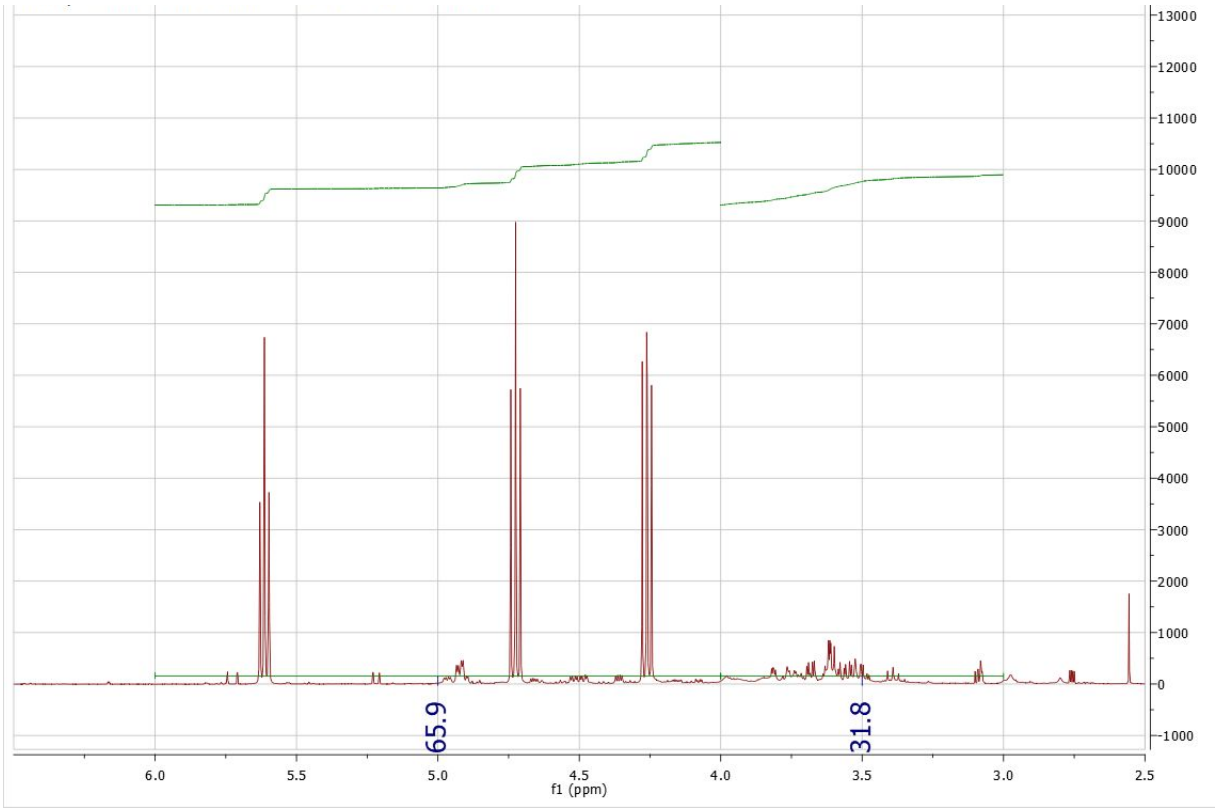

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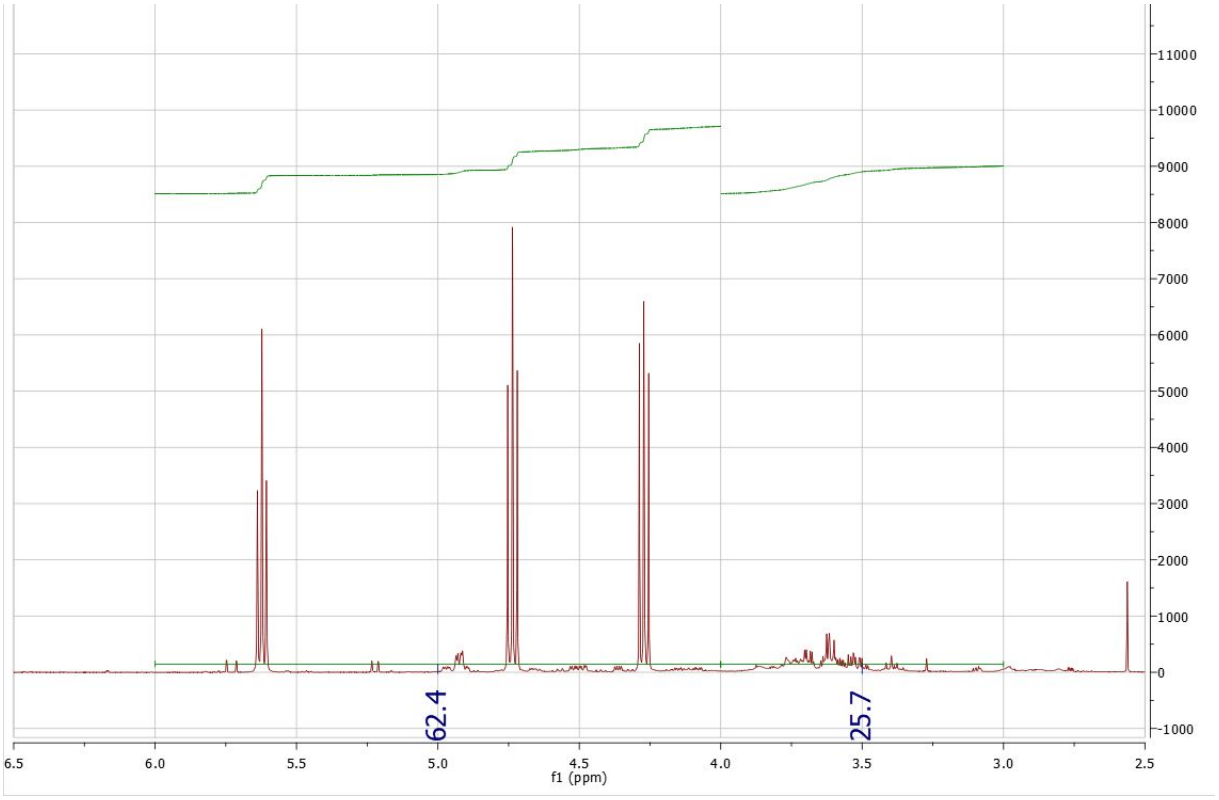
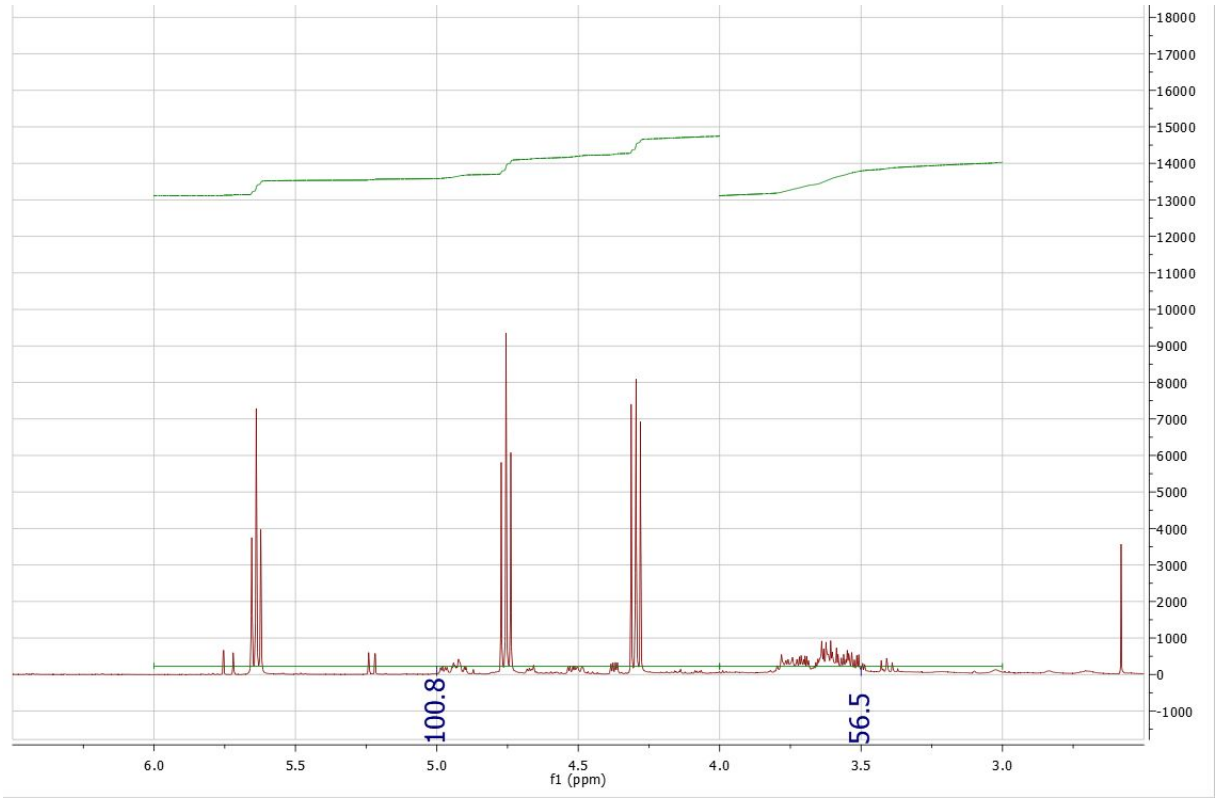
Sample V1SO155010, 1H, $CDCL_3$, 298K, 500MHz



Sample V1SO97510, 1H, $CDCL_3$, 298K, 500MHz



Sample V1SO15505, 1H, $CDCL_3$, 298K, 500MHz